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Measuring Polanyi Potentials for Chemsorb® 1000 and Chemsorb® 3800

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Polanyi adsorption potential plots are used to predict the adsorptive capacities of volatile organic compounds onto activated carbons. The design and construction of a test rig for measuring equilibrium adsorption capacities suitable for constructing Polanyi adsorption potential plots for candidate sorbents suitable for use in ECLS systems is presented. The adsorptive capacities of Chemsorb® 1000 and Chemsorb® 3800 for ethanol and acetone were measured. The capacities and Polanyi adsorption potential plots for these commercially-available sorbents were compared to that of Barnebey Sutcliffe Type 3032, an acid-impregnated activated carbon utilized aboard the International Space Station.

Nomenclature

ECLS = environmental control and life support
ISS = International Space Station
LMSC = Lockheed Missiles and Space Company
TCCS = trace contaminant control system
VOC = volatile organic compound
A = adsorption potential (mol-K/ml)
atm = pressure unit, atmosphere
C_e = equilibrium chamber concentration
C_{init} = initial chamber concentration
C = chamber concentration
d = diameter
g = gram
h = hour
l = length
L = liter
min = minute
ml = milliliter
mol = mole
P = contaminant partial pressure (atm)
P_s = contaminant saturated vapor pressure (atm)
ppm_v = part per million by volume

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q = contaminant adsorptive capacity (ml/g)
s = second
T = temperature (Kelvin)
V_m = contaminant molar volume at normal boiling point (ml/mol)
α = constant
β = constant
μmol = micromole
μl = microliter
σ = standard deviation

I. Introduction

THE control of trace contaminants from metabolic processes and material offgassing in environmental control and life support (ECLS) systems is often achieved using activated carbon beds. Since bed lifetime is determined by the adsorptive capacity of the adsorbent material for various volatile organic compounds (VOCs) found in spacecraft, accurate measurements of adsorption isotherms are needed for sizing suitable trace contaminant removal systems. In 1970, Lockheed Missiles and Space Company (LMSC) developed a rapid method based on the Polanyi adsorption potential theory for predicting the adsorption equilibrium capacities of adsorbents from commonly available adsorbent and adsorbate properties.[1] The Polanyi adsorption potential approach describes the energy relations involved in transferring gaseous molecules to the adsorbed state within micropore volumes of activated carbons and assumes a fixed volume of sorption space close to the sorbent surface.[2] Polanyi divided the adsorption process into two steps: 1) the change from the gaseous to the saturated liquid state and 2) the change in passing from the liquid state to the adsorbed state. He found that the free-energy change for first step, the adsorption potential, described the whole process, that the adsorption potential was a function of the volume of the adsorbed phase, and that the function did not change with temperature.[3]

This approach has been used to characterize the equilibrium adsorption capacities of activated carbons for VOCs and ammonia (NH_3) used by the International Space Station's (ISS) Trace Contaminant Control System (TCCS).[4] In this paper we describe the design and construction of a test rig for measuring equilibrium adsorption capacities suitable for constructing Polanyi adsorption potential plots of candidate sorbents for use in ECLS systems. The method was first validated by reproducing adsorption potential plots of ethanol for Barnebey Sutcliffe Type 3032 activated carbon and comparing it to data collected by LMSC. The method was then used to compare the efficacy of two candidate sorbents—Chemsorb® 1000 and Chemsorb® 3800—using adsorption potential plots of acetone and ethanol adsorption to decide if they are suitable for replacing the commercially obsolete Barnebey Sutcliffe Type 3032 used in the ISS TCCS. The need for identifying sorbents with similar performance characteristics helps mitigate commercial obsolescence risks which arise periodically as commercial products are no longer manufactured or are discontinued. This is especially important to enable future deep space exploration missions.

II. Materials and Methods

The following discussion presents the basic concept of adsorption potential and describes the experimental apparatus and methods.

A. Polanyi Adsorption Potential Plots

The adsorptive capacity, q, is determined under a closed loop dynamic test conditions whereby the sorbent is exposed to an initial contaminant concentration in a sealed chamber and allowed to adsorb until an equilibrium concentration is reached. The Polanyi adsorption potential plot relates the equilibrium adsorption capacity, q, with the adsorption potential, A. The adsorption capacity is define by Eq. 1 and the adsorption potential is defined by Eq. 2.

$$q = \alpha e^{-\beta A} \tag{1}$$

$$A = (T / V_m) \log_{10} (P_s/P) \tag{2}$$

In Eq. 1, α and β are constants determined from the adsorption potential plot. In Eq. 2, T is the sorbent temperature (K), V_m is the molar volume at the normal boiling point (ml/mol), P_s is the contaminant vapor pressure (atm) at T, and P is the contaminant partial pressure (atm) obtained from the equilibrium concentration. The adsorption potential is calculated from the molar volume, the vapor pressure, and the equilibrium concentration.[5]

B. Barnebey Sutcliffe Type 3032

The adsorptive capacities of Barnebey Sutcliffe Type 3032 for several VOCs and NH_3 have been characterized extensively during the development of the ISS TCCS as shown by Fig. 1. Robell reported adsorption of Barnebey-

Cheney Type BD, an untreated activated carbon under dry conditions first chosen for use in the TCCS. Due to commercial obsolescence, the Type BD carbon was no longer available when Barnebey-Cheney was purchased by Sutcliffe Waterlink in the United Kingdom, and Barnebey Sutcliffe AC, an aftermarket 12% phosphoric acid treated activated carbon, was deemed to be the replacement carbon of Type BD. The Barnebey Sutcliffe Type 3032 is a 10% phosphoric acid treated activated carbon currently used in the ISS TCCS.

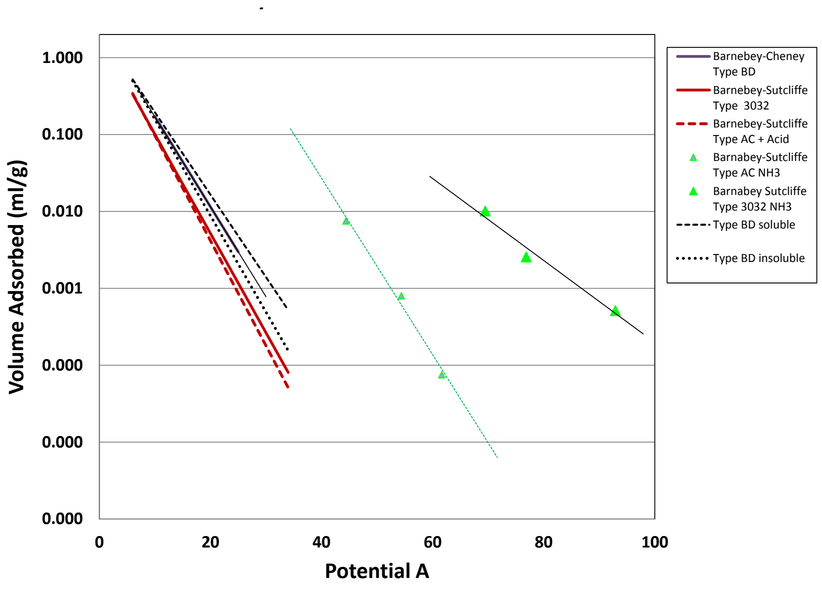

Figure 1. Comparison of Polanyi adsorption plots for Barnebey-Cheney Type BD, Barnebey Sutcliffe AC (acid treated and untreated) and acid-treated Barnebey Sutcliffe Type 3032. *Note:NH_3 curves shifted to the right.*

As seen in Fig. 1, there is variation in the relative positioning of the Polanyi adsorption potential curves for the different activated carbon products. The relative positioning, particularly NH_3, is affected by the acid treatment levels used during the manufacture of the activated carbons to enhance their capacity for NH_3 removal. In addition, the concentration of NH_3 used to test the sorbents can also play a role.

C. Closed Loop Adsorption Equilibrium Characterization System

A closed loop system shown by Figs. 2 and 3 was used for characterizing adsorption equilibrium capacities for ethanol and acetone. The system consists of a 14-liter mixing volume which includes the 0.4-liter cell of the Gasmet DX-4030 Fourier transform infrared spectrometer (FTIR), a diaphragm pump to recirculate the test gases, a fan to mix the test gases, and a bypass line with valving to divert the test gases through a 4-mm diameter tube containing the adsorbent.

The sealed mixing volume is loaded with VOCs using an adsorbent tube injection system (Supelco ATIS) that flash vaporizes a 7 – 10 µl sample into a continuous flow of an inert gas which carries the sample into the chamber. Once loaded, the VOCs are circulated through the sorbent tube and returned to the mixing volume until the equilibrium concentration is reached. The initial concentration, C_{init} (ppm_v) is recorded before circulating the VOC mixture

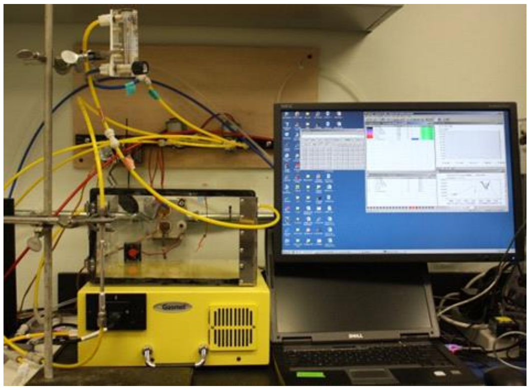

Figure 2. The closed loop adsorption equilibrium system was used to acquire data for adsorption potential plots. *The FTIR (yellow), flow meter (top left), and sorbent tube (left foreground) are visible.*

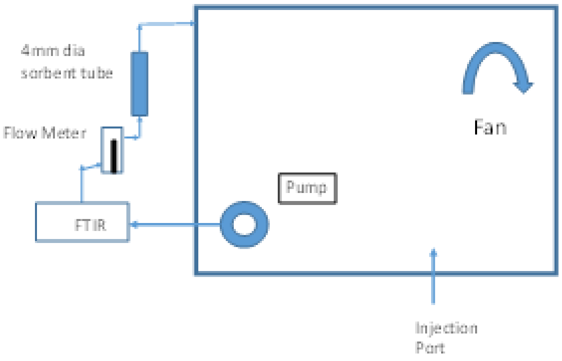

Figure 3. A simplified schematic of the closed loop adsorption equilibrium system. *The mixing chamber is dosed with a known VOC quantity and then circulated through the FTIR and sorbent tube.*

through the sorbent bed under investigation. The change in concentration is monitored every 20 seconds using the FTIR until an equilibrium concentration, C_e (ppm$_v$), is reached.

The saturation capacity for ethanol was determined using the closed loop dynamic test at ambient temperature and pressure. The chamber was filled with 100 – 250 ppm$_v$ ethanol, which was removed by 30 – 40 mg of Barnebey Sutcliffe Type 3032 activated carbon held in a sorbent tube. The ratio of chamber concentration, C, to C_{init} was plotted as a function of time as shown by Fig. 4. When the ratio becomes constant, the chamber concentration, C_e, is in equilibrium with the contaminant concentration in the adsorbed phase in the activated carbon sorbent. The Polanyi adsorption potential and the equilibrium adsorptive capacity, q, (mg/g) is derived based on data acquired at this condition.

This approach is similar to that used by Leban in 1991 except that the earlier approach used much higher concentrations and their system was apparently very well-sealed. The system used for the present evaluation was found to leak, thus a correction was applied to the adsorption equilibrium data. The method for accounting for leakage is presented by the following discussion.

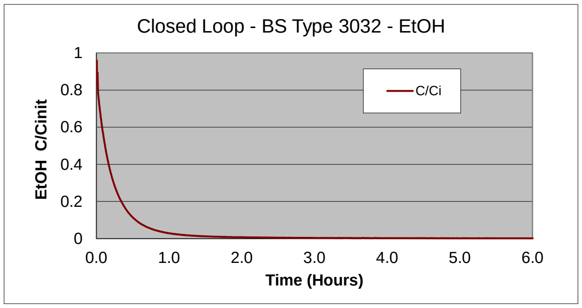

Figure 4. Mixing chamber concentration change over time for ethanol. *The equilibrium concentration (C_e) is reached when the C/C_{init} ratio is constant.*

D. Leak Correction

The concentration of trace contaminants introduced into the chamber is reduced at a constant chamber leak rate as shown by Fig 5. The concentration decreases faster when a sorbent is in the chamber because the sorbent adsorbs the trace contaminant as it flows past the sorbent at 1 L/min. The sorbent reaches equilibrium when the chamber leak rate exceeds the sorbent removal rate.

The amount of ethanol removed from the chamber increases with time as illustrated by the blue line in Fig 6. This cumulative amount is composed of the amount leaking from the chamber (red line) and the amount removed by the sorbent (green line). The total amount of ethanol (μmol) removed by the sorbent is obtained from the area under the green curve and used to calculate the equilibrium capacity, q, in mol/kg or ml/g.

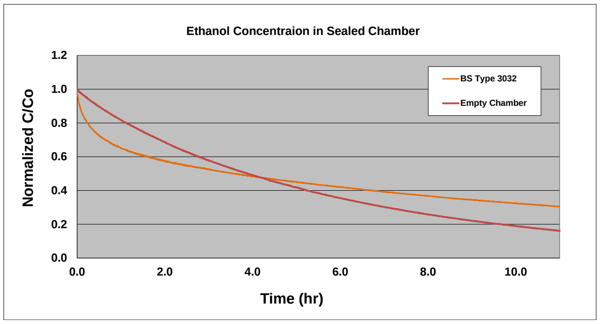

Figure 5. Closed loop dynamic test for determining adsorbent capacity. *Ethanol (270 ppmv) is introduced into a sealed chamber and the concentration decay is monitored. Ethanol removal is faster when the sorbent is in the sorbent tube than the leak rate from an empty sorbent tube. The sorbent reached equilibrium at approximately 4.2 hours.*

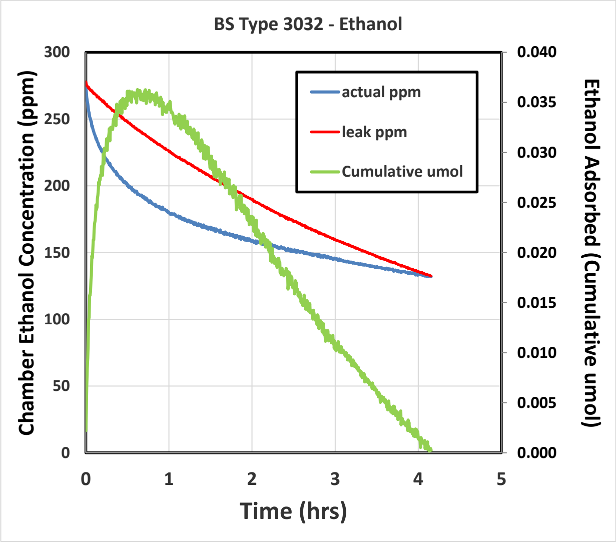

Figure 6. Leak correction of contaminant removal. *The amount of ethanol absorbed by the sorbent (green line) is the difference between the observed removal (blue line) and the amount leaking from the chamber when the sorbent is not present (red line). Equilibrium is achieved in approximately 4.2 hours.*

III. Results

Results pertaining to validating the method and constructing adsorption potential plots for two commercially-available activated carbons—Chemsorb® 1000 and Chemsorb® 3800—are presented by the following discussion.

A. Method Validation

To validate the method, equilibrium adsorption capacity results for ethanol on Barnebey Sutcliffe Type 3032 activated carbon reported by LMSC were compared to results obtained using the presently-described method. Figure 7 shows the comparison via a Polanyi adsorption potential plot. The wet and dry ethanol adsorption capacity data collected using the present method, denoted as "Ethanol KSC" in Fig. 7, fall along the adsorption potential curves reported by LMSC for Barnebey Sutcliffe Type 3032 and the after-market acid-treated Type AC carbons. This agreement provides high confidence that the methodology and the equations for determining the adsorption potential plots are valid.

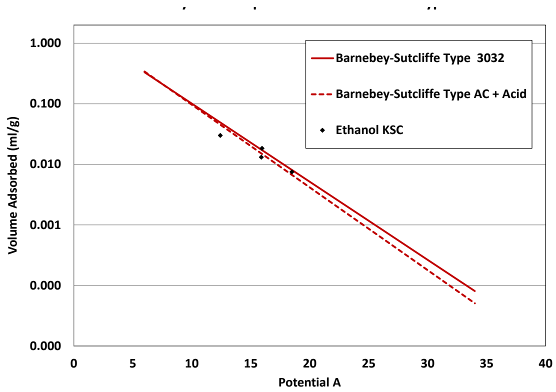

Figure 7. Polanyi adsorption potential plots for ethanol adsorption by Barnebey-Sutcliffe Type 3032. *Present results show excellent agreement with past adsorption capacity evaluation results.*

B. Commercially-Available Sorbent Characterization

Two commercially-available sorbents—Chemsorb® 1000 and Chemsorb® 3800—were evaluated for their VOC equilibrium capacity. These sorbents are products available from Molecular Products, Inc. Chemsorb® 1000 is an activated carbon derived from coconut-shell char that is intended for removal of VOCs. Chemsorb® 3800 is an impregnated activated carbon that targets VOCs, acid gases, NH_3, amines, and aldehydes.

The closed loop equilibrium adsorption capacity apparatus was used to acquire equilibrium adsorption capacity data for acetone and ethanol to construct adsorption potential plots. Figure 8 compares the Chemsorb® carbons to Barnebey Sutcliffe Type 3032. These data show that Chemsorb® 3800 has a similar performance to Barnebey-Sutcliffe Type 3032 for ethanol and acetone. The Chemsorb® 1000 has slightly better performance for ethanol and acetone than the untreated Barnebey-Cheney Type BD carbon tested by Robell. These plots suggest that Chemsorb® 1000 is better than Chemsorb® 3800 for the compounds evaluated.

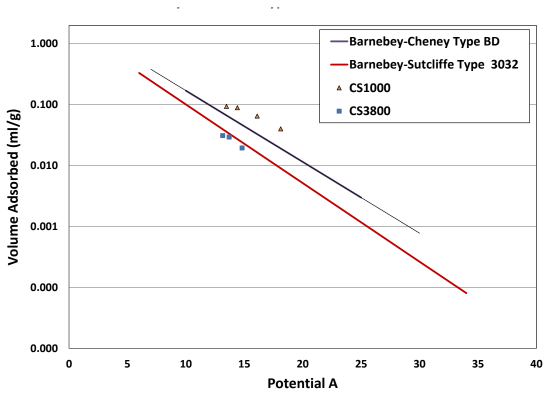

Figure 8. Chemsorb® carbons compared to Barnebey Sutcliffe Type 3032 for dry ethanol and acetone. *Triangles denote Chemsorb® 1000 and squares denote Chemsorb® 3800.*

C. Bed Design using Polanyi Adsorption Potential Data

Acquiring adsorption capacity data and constructing Polanyi adsorption potential plots for various candidate sorbents is advantageous to the TCCS designer by allowing for accurate and reliable adsorption bed sizing as well as serving as the basis for predictive bed lifetime estimates.[6] Bed dynamic adsorption capacity modeling techniques have been shown to be accurate within ±16%.[7] Because the Polanyi adsorption potential as defined by Eq. 2 accounts for temperature, adsorption capacity data acquired at a single temperature can be used to predict performance at different temperatures. This negates the need for time-consuming efforts to acquire a full range of equilibrium isotherm data. This approach saves not only time but also costs associated with acquiring data for a complete set adsorption isotherm curves but also reduces the need for iterative fabrication and testing of the adsorbent bed. Design conservatism is integrated into the design process by utilizing statistically adjusted contaminant loads (mean plus σ), including a 10-20% margin for co-adsorption effects on equilibrium capacity loading, and accounting for shifts in the adsorption potential characteristic curve caused by humidity. The rigorous bed sizing and design process based on the Polanyi adsorption potential is well described by Reference 6 and is based on Eqs. 1 and 2.[8] Herein, we briefly describe that process.

First, equilibrium adsorption capacity data are acquired using the methods described by Sections II and III. These data provide both the equilibrium capacity, q, in Eq. 1 but also the equilibrium concentration, C, in Eq. 2. Second, the adsorption potential parameter, A, is determined for the test condition using Eq. 2. To calculate A, accurate and traceable physical property data at the required system temperature and pressure must be obtained from the literature for the vapor pressure, C_s, and liquid molar volume, V_m. For instances where literature data on liquid molar volume are not available, the method of Tyn and Calus is recommended for obtaining the liquid molar volume from critical properties of fluids.[9] It should be noted that liquid molar volumes at the normal boiling point typically vary from that at room temperature by approximately 5%. The Antoine equation can be used to calculate the vapor pressure at the temperature condition. Utilizing the dataset that includes the equilibrium concentration, vapor pressure, and molar volume, values of A are determined according to Eq. 2 for each chemical contaminant of interest for the TCCS adsorbent bed design. Contaminants with a large A value will drive the sizing of the charcoal bed due to their low adsorption capacity.

Next, as a first design draft, the component with the largest adsorption potential value is used for the initial bed sizing. It follows that the adsorption capacity for this compound can then be extracted from the sorbent Polanyi adsorption potential plot. Good engineering design practice dictates that bed aspect ratios (l/d) should approximate a value of two. With this in mind, bed sizing can proceed by identifying a target bed lifetime and/or a desired TCCS performance goal.[10] Bed sizing using the equilibrium capacity alone accounts for only the bed's saturation zone length. A margin must be added to account for unusable adsorption (mass transfer zone). Velocity dependent correlations have been utilized to this end.[11]

Ultimately an iterative calculation process described by Ref. 8 that accounts for all of the contaminants of interest for the bed design is used to refine the initial design. The bed design is then validated by testing at full scale. This approach, which has been found to be a highly economical compared to acquiring a large dataset to construct a full set of equilibrium isotherm curves, has been successfully used for designing TCCS beds for both the Spacelab and ISS programs.

IV. Conclusion

The Polanyi adsorption potential methodology serves as the framework for characterizing equilibrium adsorption capacities of candidate activated carbons for controlling trace contaminants in spacecraft cabin air. The adsorption potential and the data acquired to construct adsorption potential characteristic curves has been central to trace contaminant control bed design. This approach has been utilized in sizing activated carbon beds for the Spacelab and ISS programs. Adsorption potential characteristic curves are not only useful for adsorbent bed design but also for comparing candidate replacements for the commercially-obsolete adsorbent media used in the ISS TCCS. The adsorptive capacities for ethanol and acetone of two commercially-available sorbents, Chemsorb® 1000 and Chemsorb® 3800, were used to construct Polanyi adsorption potential plots and these plots were compared to that of Barnebey Sutcliffe Type 3032, an acid-impregnated activated carbon utilized in the TCCS. This comparison suggests that Chemsorb® 1000 is a better adsorbent than Chemsorb® 3800 for the compounds evaluated.

Acknowledgments

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