

Removal of VOCs from humidified gas streams using activated carbon cloth

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This research investigates the effects of relative humidity (RH) on the adsorption of soluble (acetone) and insoluble (benzene) volatile organic compounds (VOCs) with activated carbon cloths (ACC). A gravimetric balance was used in conjunction with a gas chromatograph/mass spectrophotometer to determine the individual amounts of water and VOC adsorbed on an ACC sample. RH values from 0 to 90% and organic concentrations from 350 to 1000 ppmv were examined. The presence of water vapor in the gas-stream along with acetone (350 and 500 ppmv) had little effect on the adsorption capacity of acetone even at 90% RH. Water vapor in the gas stream had little effect on the adsorption capacity of benzene (500 ppmv) until about 65% RH, when a rapid decrease resulted in the adsorption capacity of benzene with increasing RH. This RH was also about where capillary condensation of water vapor occurs within ACC pores. Water vapor condenses within the ACC pores, making them unavailable for benzene adsorption. Increasing benzene concentration can have a significant effect on the amount of water vapor adsorbed. At 86% RH and 500 ppmv, 284 mg/g water was adsorbed, while at 86% RH and 1000 ppmv, only 165 mg/g water was adsorbed. Water vapor was more inhibitory for benzene adsorption as benzene concentration in the gas stream decreased. Copyright © 1996 Elsevier Science Ltd

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Nomenclature

A In general, the adsorption potential of a compound. Mathematically represented by $A = RT \ln(P_0/P)$

A_i Corrected adsorption potential of organic compound i considering interference with water vapor

A_i Adsorption potential of organic compound i without interference from water vapor

A_w Adsorption potential of a volume of water equal to the volume of organic compound at an adsorption potential A_i

h Fractional relative humidity (P/P_0)

P Vapor pressure

P_0 Saturation vapor pressure

R Ideal gas constant

T Temperature in Kelvin

V_i Molar volume of organic compound i

V_w Molar volume of water (18 cm³/gmol)

Introduction

Water vapor is ubiquitous in indoor environments and many types of industrial gas streams, and since it can competitively adsorb onto activated carbon cloth (ACC) or even alter the adsorption capacity of a regenerated activated carbon, it is important to understand water

vapor adsorption and its effects on ACC for the design and operation of carbon adsorption processes.

Competitive adsorption between water vapor and organics can be considered a special case of multicomponent adsorption, because water vapor is nearly always present in gas streams and it exhibits much different adsorption characteristics on active carbon than organics.

Since indoor air environments are multicomponent systems consisting of many volatile organic compounds (VOCs) and water vapor, this research examines the

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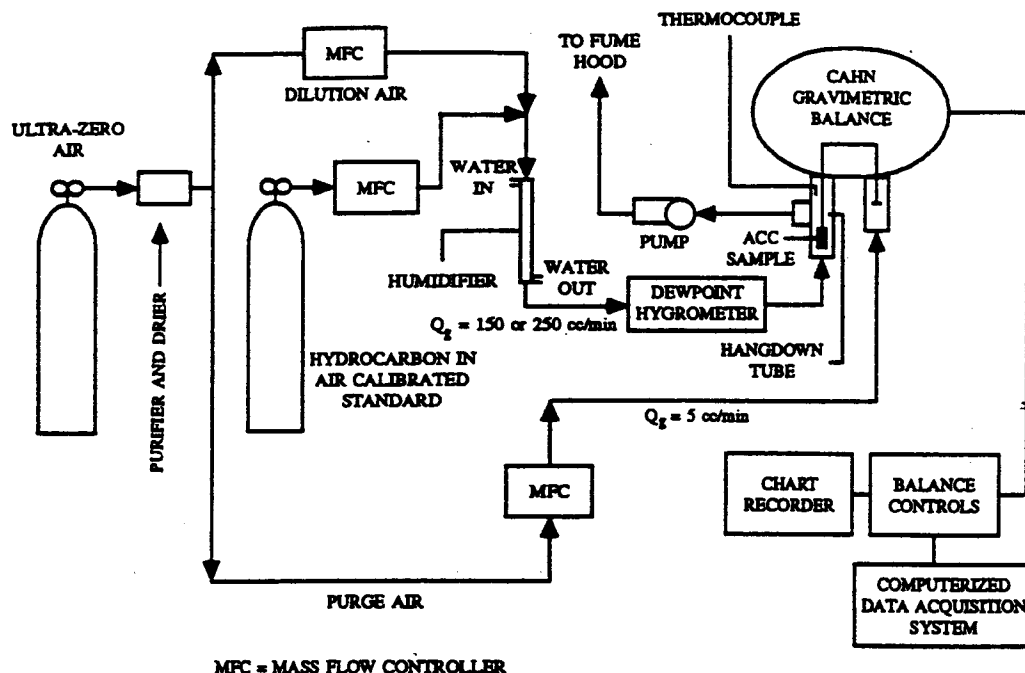


Figure 1 Experimental apparatus for measurement of VOC adsorption in humid air streams

effects of humid air on the adsorption capacity of soluble (acetone) and insoluble (benzene) VOCs. The effects of humid air on VOC adsorption are modeled with the Manes model.

Experimental methods

The experimental apparatus consisted of a custom gas generation system, a Cahn gravimetric balance (model C-2000) to measure the total mass adsorbed, a multi-ported hang-down tube on the gravimetric balance for gas sampling, and a gas chromatograph/mass spectrophotometer (Hewlett-Packard GC Model 5890 Series II, MSD Model 5971) (Figure 1)^{1,2}.

For the measurement of adsorption capacities of VOCs in humid air streams, a Gortex membrane-based humidifier was placed in the gas generation system. The humidifier consisted of a stainless steel tube with a Gortex membrane annulus. Water flowed over the outside of the membrane and the gas stream flowed on the inside of the membrane. The humidity of the gas stream was determined by the gas flow rate and the temperature of the water flowing over the membrane. A peristaltic pump was used to control the water flow rate at about 50 cm³/min. Water temperature over the membrane was varied from 4°C to 35°C to achieve relative humidities (RHs) from 35% to 90%. Relative humidity was measured with a dew point hygrometer (General Eastern). Due to the relatively large mass of the stainless steel humidifier, water at the desired temperature was passed through the humidifier for approximately one hour before the start of an experiment to establish a steady-state temperature within the humidifier. One hour was sufficient to produce steady, reproducible

RH values. The gas flow rate through the humidifier was 150 or 250 cm³/min, depending upon the experiment.

Acetone is soluble in water, and therefore some acetone is scrubbed out of the gas stream as it passes through the humidifier. At a total gas flow rate of 150 cm³/min and an inlet acetone concentration to the humidifier of 1000 ppmv, the concentration of acetone exiting the humidifier was 350 ppmv. Likewise at 250 cm³/min and 1000 ppmv of acetone entering the humidifier, 500 ppmv exited the humidifier. Benzene is insoluble in water, so the concentration entering and exiting the humidifier was the same.

Concentration of the VOC for the humidified-air/VOC experiments was measured both upstream and downstream of an ACC sample placed on the Cahn gravimetric balance. The hang-down tube on the gravimetric balance had nine ports along its side with tube fittings and GC septa (9.5 mm teflon coated). A gas-tight syringe (250 µl) was used to measure the gas-phase organic concentrations. The upstream concentration was measured 15 cm below the ACC sample in the gravimetric balance, and the downstream concentration was measured 20 cm above the ACC sample. Sampling too close downstream of the ACC sample results in an artificially low gas-phase organic concentration, due to VOC concentration gradients immediately downstream of the ACC sample. Three samples were initially taken and discarded, to clean the syringe, before the fourth sample was taken and injected into the GC/MS.

The GC/MS was calibrated and tuned before the start of each experiment. A three point calibration was used for each organic compound. The calibration points were 0, 500, and 1000 ppmv. Ten samples were taken with 500 and 1000 ppmv and related to the peak area output of

the GC/MS. The standard deviation of the samples was within 3% of the mean. Linear regression was used to relate GC/MS peak area output to gas-phase organic concentration.

During an experiment, the downstream gas-phase concentration was measured as often as the sampling procedure would allow. This meant that samples were generally taken every 2 to 3 min. The retention time for acetone on the GC column (HP-1 cross-linked methyl silicone gum) was 0.7 min at 37°C and the retention time for benzene was 1.29 min at 37°C. The total mass gain of the ACC sample was recorded using an IBM PC computer and Labtech Notebook software.

The humid-air/VOC systems examined were 350 ppmv acetone, 500 ppmv acetone, 500 ppmv benzene, and 1000 ppmv benzene at about 0, 40, 60, and 90% RH using ACC-20. The same ACC-20 sample with a mass of 0.036 g was used for all of the multicomponent adsorption experiments and was thermally regenerated before each experiment. There was no detectable change in the mass of the ACC sample after each thermal regeneration.

Multicomponent data analysis

The amount of VOC adsorbed was determined with the total adsorption capacity data (gravimetric data) and the influent and effluent gas-phase VOC concentrations. The amount of water vapor adsorbed was determined by a material balance. VOC adsorption capacity is determined by integrating the influent and effluent VOC concentrations [mg/cm^3] over the experimental run time and then taking their difference and multiplying by the total gas flow rate [cm^3/min] and dividing by the ACC sample mass [g] (Equation 1).

VOC adsorption capacity =

$$\frac{\left(\int_{t_1}^{t_2} (\text{influent})_{dt} - \int_{t_1}^{t_2} (\text{effluent})_{dt} \right) (\text{total gas flow rate})}{\text{ACC sample mass}} \quad (1)$$

Several test runs were performed using only acetone or benzene and dry air to test the above method of determining adsorption capacity. The difference between the integration method and the gravimetric measurement for a single-component adsorbate (acetone or benzene) was within 20%. The influent concentration was determined during calibration of the GC/MS and an average value was taken.

Multicomponent adsorption experimental results

Adsorption of 500 and 1000 ppmv benzene on ACC-20 at several RHs was examined. The total mass adsorbed and the adsorption capacities for benzene and water vapor are presented in Figure 2 for 500 ppmv benzene and five RH values and in Figure 3 for 1000 ppmv

benzene and four RHs. Figure 2 shows that the presence of water vapor in the gas stream does not have much of an effect on the adsorption of 500 ppmv benzene until about 65% RH, when a rapid decrease results in benzene adsorption capacity with increasing RH. This RH is also about where capillary condensation of water vapor occurs within the ACC pores. Water vapor condenses within the ACC pores, making them unavailable for benzene adsorption. As can be seen in Figure 3, increasing the benzene concentration can have a significant effect on the amount of water vapor adsorbed. At 86% RH and 500 ppmv, 284 mg water/g ACC is adsorbed, while at 86% RH and 1000 ppmv, only 165 mg/g water is adsorbed. The lower the benzene concentration, the more profound the effect of water vapor is on its adsorption capacity on ACC.

The total mass adsorbed and the adsorption capacities for acetone and water vapor are presented in Figure 4 for 500 ppmv acetone and four RHs. The presence of water vapor in the gas stream with acetone had little effect

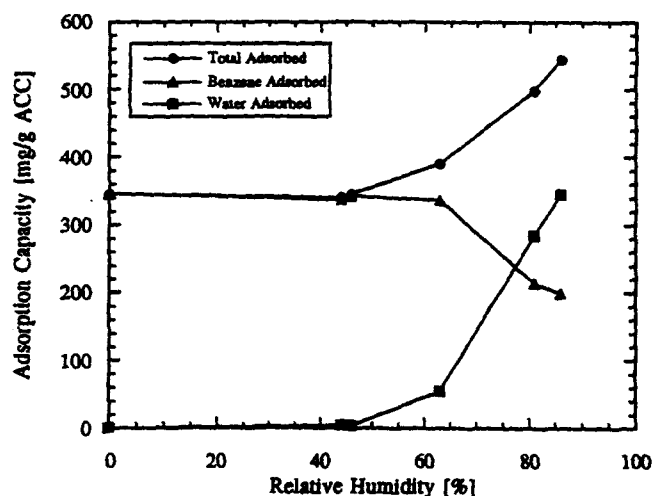


Figure 2 Adsorption capacities of 500 ppmv benzene on ACC-20 at several relative humidities

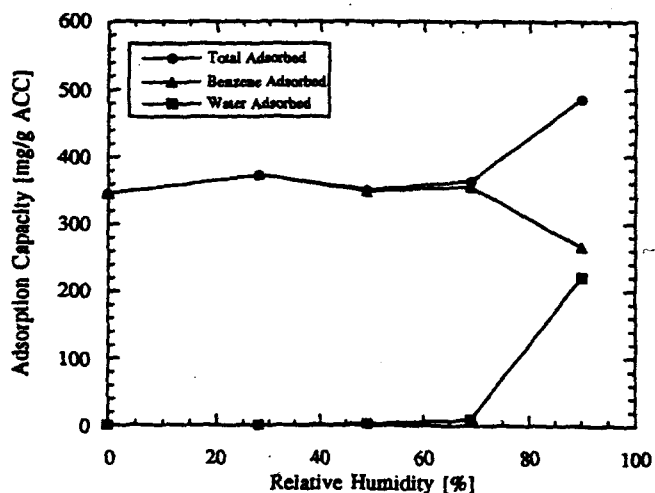


Figure 3 Adsorption capacities of 1000 ppmv benzene on ACC-20 at several relative humidities

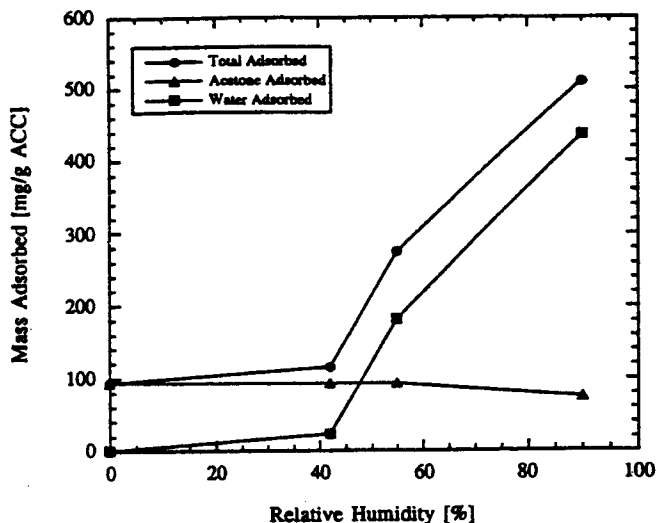


Figure 4 Adsorption capacity dependence on relative humidity of 500 ppmv acetone on ACC-20

(<20% decrease) on the adsorption capacity of acetone even at RHs of 90%. This is most likely because acetone is infinitely soluble in water, whereas benzene is insoluble and hydrophobic.

Modeling adsorption of VOCs from humid air streams

Manes³ developed a method to predict simultaneous adsorption of water vapor and organics based on Polanyi⁴ potential adsorption theory by assuming adsorbed water reduces adsorbent pore volume available for the adsorption of organic compounds on a one-to-one volume basis. Manes also assumed that the adsorption of an organic vapor at 100% RH (or $P/P_0 = 1$) was equivalent to its adsorption from an aqueous solution.

At 100% RH, the net adsorption potential for an organic adsorbate is its calculated adsorption potential without interference from water vapor (A_i) diminished by the adsorption potential of an equal volume of water (A_w) which the organic must displace from the activated carbon pores.

$$\frac{A'_i}{V_i} = \frac{A_i}{V_i} - \frac{A_w}{V_w} \quad (2)$$

where A'_i = corrected adsorption potential of component i considering interference with water vapor, V_w = molar volume of water (18 cm³/gmol), and V_i is the molar volume of the organic compound.

Equation 2 applies to any immiscible organic assuming that the adsorbed organic volume is less than the volume of the adsorbed water³. If the organic volume is greater than the volume of water, the model assumes no interferences from the presence of water. Adsorption isotherms for the pure organic vapor and for water vapor are required to use the Manes method. If the RH is less than 100%, an additional term is required to

describe the effect of water vapor on organic adsorption, as shown in Equation 3:

$$\frac{A'_i}{V_i} = \frac{A_i}{V_i} - \frac{A_w}{V_w} - RT \ln \frac{h}{V_w} \quad (3)$$

where h is the fractional relative humidity (P/P_0).

The method of Manes was used to model the adsorption of acetone and benzene under several RHs. The method of solution for the Manes model is somewhat tedious, as it requires a graphical approach. It would be possible to solve the solution numerically, if one had an adsorption isotherm equation that would fit the entire water vapor isotherm. One could then set up a system of nonlinear equations to solve for the equal volumetric adsorption capacities of the water vapor and the organic and obtain the corresponding normalized adsorption potentials (A/V).

Results from using the Manes model with experimental data for benzene are presented in Figure 5. Modeled results are presented for 0%, 65%, and 85% RH. The adsorption isotherm for 0% RH, or pure benzene, was obtained from experimental measurements in the 10 to 1000 ppmv range and extended to other concentrations using the Dubinin-Radushkevich (DR) equation^{1,2}. Experimental data points in the range of 28% to 90% RH are presented with the modeled data in Figure 5. The Manes model produced a reasonable estimation of the benzene-water absorption capacities. As discussed previously, the Manes method applies only to immiscible organics, such as benzene, so the modeled results for the acetone-water system using the Manes model are not presented.

Conclusions

The effects of humid air on the adsorption capacity of soluble (acetone) and insoluble (benzene) compounds on activated carbon cloth (ACC) were characterized with

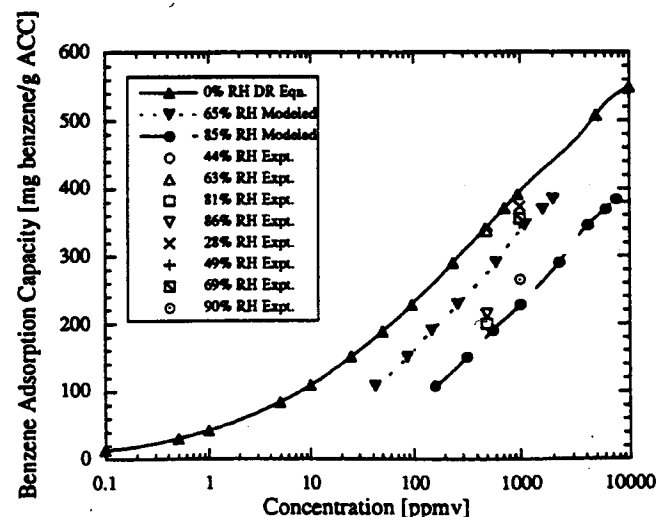


Figure 5 Measured and modeled results for benzene adsorption on ACC-20 at various relative humidities

this research. Acetone showed little decrease in its adsorption capacity on ACC, up to about 90% RH, while water vapor had an effect on benzene adsorption starting around 65% RH, and became more pronounced as RH increased. As benzene concentration was increased, the diminishing of benzene adsorption capacity due to increased RH lessened.

Acknowledgements

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