Surface Measurement Systems
World Leader in Sorption Science

DVS
Application
Note 65

Impact of Relative Humidity on the Adsorption of Volatile Organic Compounds by Porous Materials –Two Component Sorption Study

Majid Naderi[1], Manaswini Acharya[1], Meishan Guo[1], Damiano Cattaneo[1], Elwin Hunter-Sellars[2], Daryl R. Williams[2] and Daniel Burnett[1]

[1]Surface Measurement Systems Ltd.

[2]Department of Chemical Engineering, Imperial College, London, UK.

This application note is based on recent publications by Elwin Hunter-Sellars et al. [1],[2] and will focus on the removal of volatile organic compounds by porous inorganic solids. A range of pore size distributions and chemistries were assessed at room temperature and relative humidity (RH) values from 0 to 70% to reflect real-world conditions similar to those of indoor air. Dry removal performance appeared to be dependent on the surface area of adsorbents and, for polar compounds, the relative hydrophobicity of the material. Performance of sorbents with hydrophilic surface chemistry, such as silica gel and molecular sieve 13X, decreased drastically with small increases in pre-exposed humidity. Activated charcoal and high-silica faujasite Y retained their capacities for toluene in relative humidities up to 50% and 70% respectively, which highlights their selectivity for non-polar species due to hydrophobic pore structure and low water vapour uptake.

Introduction

The presence of pollutants in the air is becoming an area of significant interest and there has been an increasing concern about air quality and its impact on health due to the presence of volatile organic compounds (VOCs) in the air. Volatile organic compounds can be released from a wide range of sources including inside the houses and industrial places. Concerns have recently moved from environmental impacts to a health problem and increased levels of VOCs have been affiliated with respiratory and pulmonary diseases. VOC molecules include toluene, formaldehyde, methylene chloride, tetrachloroethylene, xylene, acetone and benzene which may appear in different forms in solvents, paints or packaging materials. It is therefore important to find a solution for the removal of volatile organic pollutants from the air.

Porous materials are considered a cost effective route to capture VOC pollutants and the reason for their success is the high fraction of pore volume and adsorption sites for trapping volatile species. Researchers have focused on the synthesis and design of porous adsorbents with high surface areas including metal organic frameworks, porous polymers and mixed matrix membranes. However, zeolites and activated carbons are widely used due to their low cost and wide spread availability.

P-SCI-469v1.0 Dec 2020

VOC concentrations can vary in different environments but are significantly lower than the moisture concentration. Therefore, water molecules would be competing for the same adsorption sites as VOCs and it would be important to assess the impact of humidity on the choice of porous material for removing certain VOC molecules. There are different phenomena as to how water sorption takes place and where the water molecules can sorb. They can form monolayer or multilayer on the surface of the substrate, condense inside pores, absorb into the bulk or form a chemical reaction.

This study will look at the impact of humidity on a series of common industrial porous materials which are potentially used for capturing VOCs. Single component experiments using water or organic vapour molecules as well as a combination of both components water and organic vapour have been studied. All the experiments were performed at 25°C.

Method

In the Dynamic Vapour Sorption (DVS) technique a saturated carrier gas flows over a sample. As the sample is exposed to the vapor molecules there will be a change in the mass. As the vapor concentration is increased there are more vapor molecules present and the sample shows an increase in mass. The sorption isotherms can then be plotted by using the mass data against the relative vapor pressure of the solvent.

Single-component adsorption measurements

Adsorption isotherms of all volatile species (toluene, 2-butanone, ethanol) as well as water vapour, were carried out gravimetrically using a DVS Endeavour at 25°C and atmospheric pressure, using 300 ml/min of dry air as the carrier gas. Vapour concentrations were measured and maintained using closed-loop control of speed-of-sound (SOS) sensors, with the lowest relative pressure of vapour studied being $P/P_0 = 0.005$. Samples weighing between 40 and 80 mg were activated at 300°C for 3 h before being held under dry airflow at 25°C until their masses remained constant.

Two-component adsorption measurements

Humid adsorption measurements (water + toluene, water + ethanol) utilised the dual-solvent mode of the DVS Endeavour. Following pre-preparation and drying, samples were equilibrated with different levels of humidity, before introducing a step change of $P/P_0 = 0.005$ in volatile concentration while maintaining the same humidity level. The final adsorbed quantity of VOC was calculated by subtracting the mass increase following water adsorption from the total mass uptake of the dry sample in the course of the experiment, assuming no loss of water adsorption. The carrier gas for this process was dry air in all cases, using a total flow rate of 300 ml/min. This experiment represents the 'wet adsorbent' mode of competitive adsorption, where the volatile species bond to unoccupied sites, or attempt to displace pre-adsorbed water present on the material. A similar method has been utilised for studying the impact of humidity on CO_2 adsorption by metal organic frameworks[3]. As gravimetric sorption analysis of a two-component vapour stream quantifies the total amount of sorption, any measurements of humid performance must consider this limitation and be considered only semi-quantitative, even when reproducible. In all experiments, the relative pressure of water exceeded that of the VOC by at least 20 times in order to reduce the effect of competition on the reproducibility of results.

Results

Table 1 shows the commonly used adsorbents with hydrophilic and hydrophobic surface chemistries tested for adsorption by polar and non-polar VOCs. Activated carbon (AC), amorphous silica (AS), zeolite 13X (MS13X), zeolite Y (A88Y) and ZSM-5 (A14Z) were studied.

Table 1: *Surface properties of adsorbents: molecular sieve 13X (MS13X), zeolite Y (A88Y), ZSM-5 zeolite (A14Z), activated carbon (AC) and amorphous silica (AS). Determined using N_2 sorption at -196°C.*

Adsorbent	SiO_2:AlO_3 [mol/mol]	Surface area [m^2/g]	Hydrophilicity	Porosity
AC	N/A	1245	Hydrophobic	Micro/ Mesoporous
AS	>2000	338	Hydrophilic	Mesoporous
MS13X	1.9	666	Hydrophilic	Microporous
A88Y	35.8	659	Hydrophobic	Micro/ Mesoporous
A14Z	29.7	413	Hydrophilic	Micro/ Mesoporous

Powder X-ray Diffractions showed crystalline zeolites. Thermal Gravimetric Analysis data (not shown) showed mass losses at below 200°C and above 600°C due to removal of water and chemical decomposition, respectively.

Table 1 shows nitrogen sorption analysis of the samples which established the surface area and micro/mesoporous characteristics of the samples.

Single-component DVS isotherms are shown in Figure 1. The water sorption isotherms show that MS13X has the greatest affinity for water. Toluene sorption isotherms (Figure 1b) illustrate a different behaviour where AC sample picks up a substantial amount of toluene whereas MS13X has a much smaller uptake. Considering the uptakes of all the organic vapours it can be concluded that moving from a polar molecule like water to a relatively non-polar molecule there is a significant difference in single component uptakes where activated carbon (AC) shows the most uptake for the organic vapours. However, further two component sorption studies suggest otherwise.

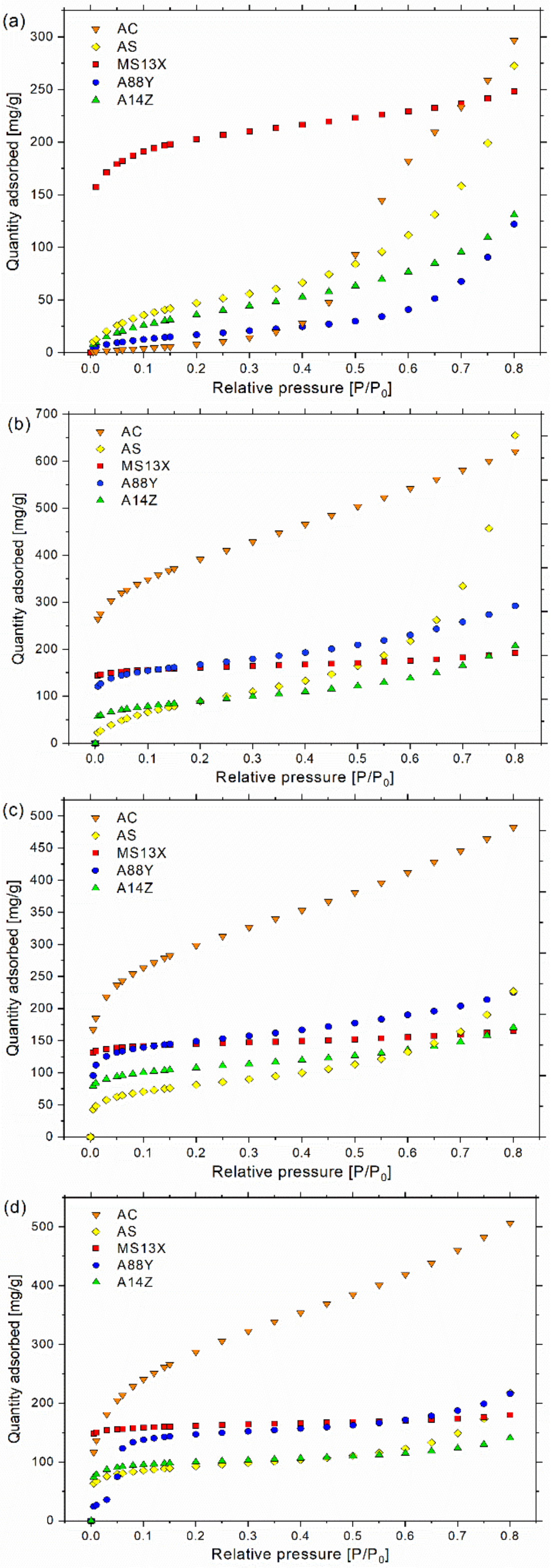

Figure 1. *Gas-solid adsorption isotherms for (a) water, (b) toluene, (c) 2-butanone, and (d) ethanol. All measurements carried out at atmospheric pressure under dry air flow of 300 ml/min and 25°C.*

Table 2: *Summary of adsorbed vapour amounts by adsorbents: MS13X, A88Y, A14Z, AC and AS. Determined gravimetrically in single-solvent mode at 25°C.*

Adsorbate	Quantity adsorbed [mg/g][a]				
	AC	AS	MS13X	A88Y	A14Z
Water	1.7	10.9	158.1	5.3	8.7
Toluene	264.1	21.2	145.4	120.6	57.4
2-Butanone	167.2	43.0	131.6	95.8	79.5
Ethanol	113.8	61.7	148.2	24.0	73.2

[a] Relative pressure of adsorbate, $P/P_0 = 0.005$.

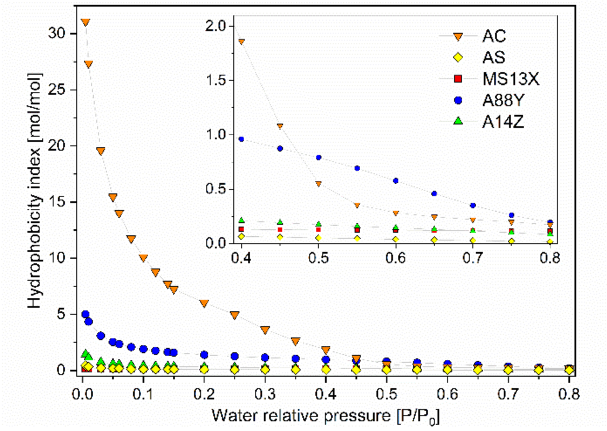

Figure 2. *Hydrophobicity indexes (HI) as a function of water relative pressures. HI is calculated using single-component capacities of toluene at relative pressure of 0.005 P/P_0 and capacities of water vapour at various relative pressures. Inset displays values at water relative pressures exceeding 0.4 P/P_0 for clarity.*

Table 2 summarises the adsorbed vapour amounts by the adsorbents tested at one concentration (P/P_0=0.005). A simple screening study using single component sorption studies would therefore suggest that activated carbon (AC) would be the best adsorbent for removing the above organic vapours. From Table 2 the single component data may be used to create a hydrophobicity index (HI) where the uptake of toluene at a fixed concentration was compared at different relative humidities. Figure 2 shows that in terms of hydrophobicity the activated carbon material appears to be the most hydrophobic material and at low %RH values shows the highest uptake of toluene. However, at relatively higher concentrations of water zeolite Y (A88Y) shows higher toluene uptake.

The above results were based on single component studies. However, in real-world conditions both water and toluene molecules are competing for the porous materials. In general, two-component adsorption interactions can be divided into two phenomena: co-adsorption, where the species interact with different adsorption sites; and competitive adsorption, where they occupy and compete for the same adsorption sites. Figure 3 shows two-component DVS data where impact of humidity on adsorption of toluene and ethanol by the adsorbents has been studied by determining the amount of adsorbed toluene at 0, 10, 30, 50, and 70 %RH to represent both high and low humidity conditions. MS13X is the best example for competitive adsorption, as its capacity for both toluene and ethanol dropped to negligible levels following exposure to water vapour. Under dry conditions (0% RH) activated carbon takes up a significant amount of toluene (over 25%) as expected. Even at 10-30% RH the performance of activated carbon is greater than the other adsorbents. But, moving to 70% RH the toluene uptake drops by a factor of ten. Therefore, whereas activated carbon would be ideal for removing VOCs in dry conditions it would not be ideal adsorbent for removing VOCs in a tropical environment. The interesting performance comes from zeolite Y where the uptake was relatively lower than activated carbon (12.5%), but its performance was independent of relative humidity. The hydrophobic sites in zeolite Y are ideal for VOCs and they are not compromised by water vapour molecules, as predicted by the hydrophobicity indexes calculated previously.

In order to study the reproducibility of the sorption experiments and the regeneration of the adsorbents, adsorption-desorption cycling experiments were carried out using the DVS Endeavour and similar experimental conditions to the isotherm measurements. Adsorbed quantities were calculated using the change in mass between the ends of the current cycle's adsorption and previous cycle's desorption step.

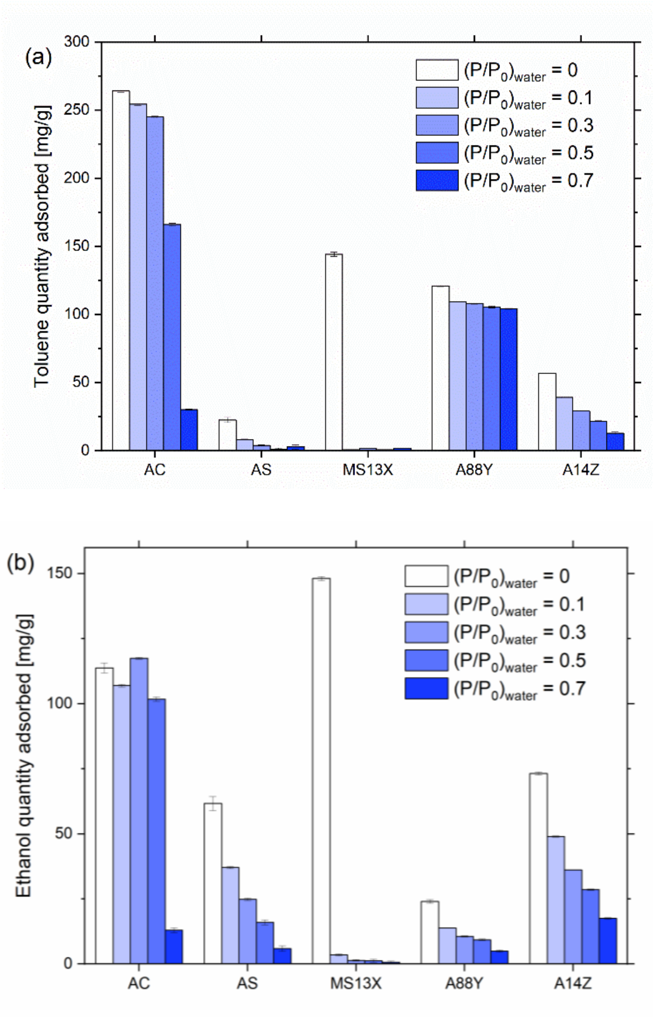

Figure 3. *Adsorption capacities for toluene (a) and ethanol (b) after exposure to humidity, measured using two-solvent gravimetric experiments. Relative pressure of volatile in all experiments was 0.005 P/P_0. T = 25°C.*

Figure 4 shows multi-cycle adsorption experiments for toluene vapour at 0 and 50% RH conditions where reproducible behaviour can be seen for most adsorbents except activated carbon which lost 35% performance during the regeneration, identical to that of the dry cycling experiments. Regeneration studies on activated carbon have shown decreases in adsorption capacity with increasing cycle time due to pore blockage, and often utilise high temperature or vacuum conditions for regeneration. Zeolite Y maintained a relative performance of over 98% in all studied cycles, allowing it to adsorb quantities of toluene similar to activated carbon under these conditions. The trends observed suggest the role of water vapour in regeneration and adsorption cycling behaviour depends on the adsorbent's surface chemistry and pore structure, as well as the preferred bonding sites of water and toluene molecules.

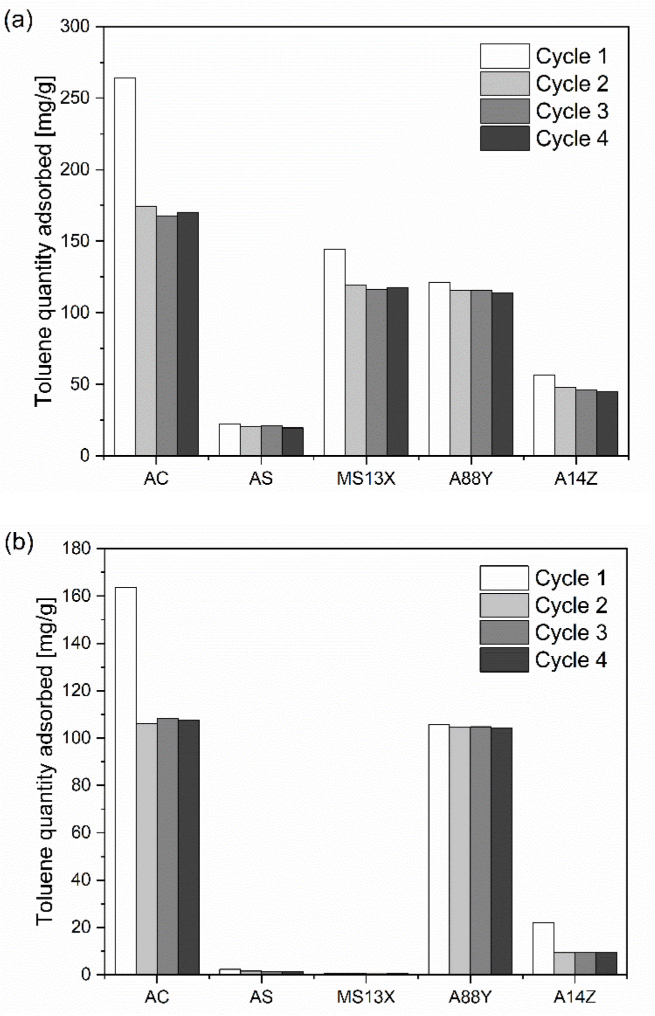

Figure 4. *Quantities of toluene adsorbed as a function of cycle number, under dry (a) and humid (b) conditions. Relative pressure of toluene in all cycling experiments, P/P_0 = 0.005. Relative pressure of water in humid experiments, P/P_0 = 0.5. Desorption carried out under 200 mL/min of dry air flow, T = 25°C.*

Conclusion

Single component adsorption studies provide some guidance on choice of the best adsorbents, but two components experiments provide definitive data for VOC adsorption in the presence of a range of relative humidities.

Humidity impacts performance as the adsorption performance of an adsorbent material for capturing of organic vapours when humidity is not present, is usually far worse than when humidity is present. The performance of Zeolite Y under dry air conditions for organic vapours is very average, but under humid conditions it outperformed the other adsorbents for various organic species. Its success can be ascribed to its hydrophobic surface properties.

DVS instruments are able to run competitive water – organic vapour experiments and multi cycling experiments allowing real-world adsorption behaviour to be quantified.

References

[1] Elwin Hunter-Sellars, J.J. Tee, Ivan P. Parkin, Daryl R. Williams, Adsorption of volatile organic compounds by industrial porous materials: Impact of relative, Microporous Mesoporous Mater. 298 (2020) 110090.

[2] Elwin Hunter-Sellars, Paola A. Saenz-Cavazos, Anthony R. Houghton, Sean R. McIntyre, Ivan P. Parkin, Daryl R. Williams, Sol–Gel Synthesis of High-Density Zeolitic Imidazolate Framework Monoliths via Ligand Assisted Methods: Exceptional Porosity, Hydrophobicity, and Applications in Vapor Adsorption, Adv. Funct. Mater. (2020) 2008357.

[3] N. Chanut, S. Bourrelly, B. Kuchta, C. Serre, J.S. Chang, P.A. Wright, P.L. Llewellyn, Screening the effect of water vapour on gas adsorption performance: application to CO_2 capture from flue gas in metal–organic frameworks, ChemSusChem 10 (2017) 1543–1553.