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Method and kit for adsorbent performance evaluation

Neil A. Stephenson · Steven J. Pontonio · Michael T. Freiert · Rachael A. Masin · Philip A. Barrett

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Abstract Commercial gas separation plants running adsorption processes, including pressure swing adsorption, vacuum pressure swing adsorption and temperature swing adsorption are intended to operate continuously and meet design performance levels over the complete service life of the facility. Performance degradation of the adsorbent materials in extended commercial usage is a common problem. Issues such as adsorbent aging and poisoning by unwanted or unexpected contaminants, represent some of the causes of declining adsorbent performance. Lower adsorption capacity can result in declining productivity and/or product purity for the gas separation plant. Adsorbent troubleshooting is usually accomplished by taking samples from the plant and sending them to off-site laboratories for analyses such as moisture content determination by Karl Fischer titration, or BET surface area or other adsorption capacity measurements. The turnaround time for these laboratory analyses is on the order of days. To short-cut this lengthy process of analysis, we have developed a simple test method and kit for rapid diagnosis of adsorbent performance issues which can be used directly at a plant site. The test method involves the determination of the gas capacity of an adsorbent by equilibrating the adsorbent with an appropriate test gas, deactivating the adsorbent and measuring the amount of test gas released. Once a sample has been acquired, the test can be executed and results obtained in less than 15 min. We show that the test method is accurate to within 5 % of the adsorption capacity determined from isotherm measurements, at equivalent temperature and pressure, and can be used to test common commercial adsorbent types, including low silica zeolites and activated carbons.

Keywords Adsorbent performance · Test method · Test kit

N. A. Stephenson · S. J. Pontonio · M. T. Freiert · R. A. Masin · P. A. Barrett (✉)
Praxair, Inc., 175 East Park Drive, Tonawanda, NY 14150, USA
e-mail: philip_barrett@praxair.com

1 Introduction

One of the challenges of maintaining a commercial gas separation plant, employing adsorption technologies (Sircar and Myers 2003) is determining whether or not the adsorbent is in the desired condition for the process. In commercial service it is not uncommon for the adsorbent performance to degrade over time. Unwanted or unexpected contaminants in the gas stream or entering the adsorbent vessels through leak points, natural aging and loss of surface area over time and/or damage by exposure to excessive temperatures are all common causes of reduced adsorbent performance. When a reduction in plant performance is detected, for example by a loss of purity or by decrease in productivity, the common course of action is to take samples from the operating plant and send these to specialized laboratories for analyses. A very large number of laboratory based methods and techniques have been developed to study adsorbent materials and determine amongst other things their chemical make-up, physical properties and adsorption characteristics (Webb and Orr 1997). Measurements such as adsorption isotherms, adsorption kinetics (Ackley and Leavitt 2002), surface area characterization (Brunauer et al. 1938) and residual moisture content analyses (MacLeod 1991) are routinely used to determine the applicability of a given adsorbent to carry-out a particular separation. As a result, these tests often form a part of the specifications for commercially available

adsorbent products. For all of the tests and test methods listed above, specialized laboratory equipment and a skilled operator are required and in each case, the measurement time is on the order of hours. As a result, it can take several days, including time for sample collection and shipment to a specialized laboratory, to determine whether or not adsorbent from a commercial gas separation plant has been degraded in any way that reduces plant performance.

A clear unmet need was to develop a field test method and associated test equipment to enable timely diagnosis of adsorbent performance issues directly at the plant site (Stephenson et al. 2008). It was important for this test method to be reliable, since important decisions, such as whether or not a plant needs to be reloaded, could be made based on these field test results. High throughput was another desirable feature to enable multiple samples to be analyzed from different adsorbent beds and/or from different locations within an adsorbent bed. A test method that enabled more sample analyses from a given gas separation plant would help understand the extent of any adsorbent damage and/or contamination and perhaps enable the source to be identified and similar issues avoided thereafter. Given that many commercial plants are in remote locations, it was considered that any complex analytical equipment, especially components requiring frequent calibrations, should be avoided. A final request was to reduce the test method to practice in a "simple to use" kit form with minimal consumables to enable plant staff, as opposed to adsorption experts, to execute the test and interpret the data for themselves. Meeting this final request was considered essential to ensure widespread usage of this test and method at commercial sites around the world.

The field test method that has been developed is not adsorbent specific and can be used to assess any adsorbent from any adsorption process, in principle. The pre-requisite for its use is that either the performance of a functioning sample is known and/or that a suitable reference sample is available, from which performance comparisons can be made. An attractive feature of the test is that an adsorption capacity is obtained directly since, for most adsorption processes, the adsorption capacity is very diagnostic of performance.

2 Test method and test equipment

The fundamental premise behind the test method is the pre-saturation of an adsorbent sample with a test gas and use of a displacing agent to release any adsorbed test gas from the adsorbent sample and provide a means to capture this evolved test gas for quantification, in terms of amount released per gram of sample. The displacing agent can be anything that is capable of "displacing" and thereby releasing the adsorbed test gas from the sample. Since many commercial adsorption processes use low silica zeolites, especially X and A types, and given that these zeolites are very hydrophilic (Pfenninger 1999), water is an excellent displacing agent for these types of materials, particularly when common atmospheric gases are used as the source of the pre-adsorbed test gas. The generic steps involved in carrying-out this test method are as follows:

1. Collect adsorbent sample(s) from plant or process
2. Saturate sample with test gas under a controlled environment
3. Measure sample weight and sample temperature
4. Deactivate sample with displacing agent
5. Measure volume (ml) of test gas evolved
6. Compute adsorption capacity in ml/g

The above sequence, steps 1–6 applies to cases wherein the same gas is used for both the controlled environment and for the test itself. In cases where the test gas is different to the gas used to provide the controlled environment (see case study 2 below), steps 2 and 3 are reversed and the adsorbent sample is weighed and handled in the controlled environment and purged with the other test gas in a separate step. In this latter type of test where the test gas is different to that used for the controlled environment, the sample temperature is still measured after equilibration with the test gas.

The simplicity of this test method makes it compatible with a number of different types of equipment which could be used to carry out the test. However, since our objective was to create a robust, field compatible test, we found that the following basic equipment choices offer the best balance between ease of use and suitability for field use:

1. Glove bag to provide a controlled environment for sample transfer, handling and for some adsorbent samples, saturation with the test gas
2. Weighing scale and infrared thermometer for sample weight and temperature measurement
3. Sample vials with caps containing a septum which are used to house samples pre-saturated with test gas and/or saturate the samples with test gas in situ prior to test execution
4. A glass syringe with needle and scale to inject the displacing agent into the sample vials and in turn, to collect and measure the volume of test gas evolved. The syringe should be sized to capture all the test gas expected to be released from the sample and should have a graduated scale on the side for volume measurement. A preferred type of syringe is a conventional glass syringe equipped with a plunger having a ground-glass barrel. This type of syringe is preferred, since the ground-glass barrel offers a low friction

movement which doesn't require significant pressure to move the plunger back. Although this style of syringe is not necessarily gas-tight, it functions very well, since common liquid displacing agents, such as water, provide a natural seal and thereby avoid any loss of evolved test gas.

2.1 Sample collection from plant or process

The process adopted to remove the sample from the adsorber vessels at the plant site is independent of test method and the same procedure is used for both the field test method described herein, as well as for samples sent off-site for conventional laboratory analyses. For any of these tests, the same level of care is required to obtain representative samples from the plant or process, and maintain these in their "in plant" or "in process" state. An adsorbent sample is taken from selected locations within the vessel and is handled and stored to prevent any additional contamination and/or damage. For example, zeolite adsorbents can be extremely hydrophilic and even a short exposure to ambient air can allow moisture to be adsorbed. Therefore, the test sample is handled in a controlled environment such as a glove bag inflated with a suitable dry gas such as nitrogen or instrument air.

2.2 Saturation of sample with test gas under controlled environment

The test gas selection is tied to a particular adsorbent and service, since the optimal choice quantifies performance in the target application. The gas used should be one that is readily available in dry form and which is appreciably adsorbed by the adsorbent. For the purposes of the test, the gas does not necessarily need to be in a pure component form, and commonly available multicomponent gases such as dry air can be used. In addition, it is convenient to design and set-up the test such that the volume of gas released is on the order of 50 ml for a sample weight of a few grams. Gas volume and sample weights of these approximate magnitudes are convenient to measure with the required precision. As an example, to test a nitrogen-selective zeolite such as Li–LSX used in vacuum pressure swing adsorption (VPSA) air separation plants to produce oxygen, suitable test gases are dry air or nitrogen. These are particularly convenient since they can be used directly to purge the controlled environment (e.g. glove bag) during sample handling and sample weighing and therefore no further equilibration step is needed.

Equilibration is controlled primarily by using a minimum time for saturation of the adsorbent with the test gas. To set a minimum equilibration time some knowledge of the adsorption kinetics for the adsorbent sample is required. Our motivation to develop this test method was primarily to determine adsorption capacities for commercial adsorbents from our gas separation plants using common gases, especially atmospheric gases. For these gases and these adsorbents, we have accurately determined the adsorption kinetics using breakthrough and other measurements and these data have enabled us to set minimum times for equilibration for our commercial adsorbents with these common atmospheric gases. In addition to the time criteria, we also use temperature measurements provided from an infrared thermometer to provide a second measurement that equilibration has been achieved by monitoring the sample temperature as a function of time and ensuring this has reached a stable value. Adsorbents and/or types of gases which require very long equilibration times (e.g. on the order of hours or more) fall outside the scope of this test method, as originally conceived. For samples with unknown kinetics, the recommendation is to run a series of tests at different equilibration times to determine the impact of equilibration time on the measured adsorption capacity. The simplicity of the test and test equipment make running repeat tests at longer equilibration times straightforward. For samples and test gases that require very long equilibration times, useful information may still be obtained from running the test after a fixed amount of equilibration time and accepting that the sample may not be fully saturated. By comparing a series of samples treated under identical conditions, qualitative information regarding the performance of the adsorbent samples, compared to suitable reference examples, can still be obtained.

For other applications, including air prepurification using 13X zeolite or for adsorbents with low nitrogen or dry air adsorption capacities, a test gas such as CO_2 can be used. In this case, the sample is transferred within a controlled environment (nitrogen or dry air) as described above and then sealed. Equilibration with CO_2 must then be accomplished in a separate step. The sample vial having a septum lid provides a way to accomplish this by introducing a CO_2 purge into and through the vial using a needle inserted through the septum, connected to a CO_2 source and a second needle which is open to atmosphere can serve as a vent line and maintains ambient pressure (Fig. 1). The purge is continued for several minutes, as dictated by the adsorbent kinetics and the sample temperature is measured in order to verify that this has stabilized at ambient. The sample temperature is conveniently measured using an infrared thermometer with a digital scale that can be handled comfortably within the controlled environment. At this point, the two needle connections (one to the CO_2 source and the other acting as the vent line) can be removed, since at this point the sample will be saturated in the CO_2 test gas.

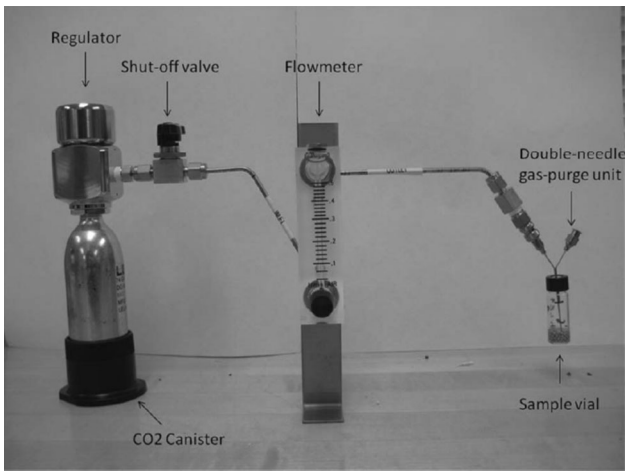

Fig. 1 Photograph showing equipment and configuration for saturating an adsorbent sample with CO_2 test gas

2.3 Sample weight and temperature measurement

For tests using gases which were employed in step 2.2 to provide the controlled environment, the weight measurement is made after saturating the sample with the test gas. As such, the weight measurement reflects both the sample mass as well as, the mass of test gas adsorbed by the sample. This "test gas loaded" sample weight is different to the "unloaded" weight used in most conventional isotherm measurements. To enable comparison with isotherm measurements using "unloaded" sample weights, a correction can be applied to the sample weight, after the test has been executed and the volume of test gas released from the sample is known. This volume of test gas can be converted to a weight percent value and this weight percent value can be used to calculate the mass of adsorbent test gas stored on the adsorbent which can be subtracted from the original "test-gas-loaded" sample weight, to yield a corrected sample weight that closely approximates the "unloaded" sample weight used in conventional isotherm measurements. The impact of this weight correction is discussed in Sect. 3. For tests with gases other than those used for the controlled environment (e.g. case study 2 using CO_2), applying a weight correction is more complicated, since for a given sample two tests are required, a first test to determine the amount of the controlled atmosphere gas stored on the sample for the weight correction, and a second test using the actual test gas. In practice we have found that weight corrections are not typically needed, especially in cases where samples of the same type are being compared at field locations to estimate whether any of them have inferior adsorption capacities. Weight corrections of the type discussed are generally only required to compare these field test data to isotherm or other adsorption capacity measurements, wherein the sample weight for the comparative data is an activated or "unloaded" sample weight.

The weight is recorded to enable the amount of gas evolved in the next part of the test to be expressed on a per gram of sample basis. At this stage, the sample temperature should also be recorded, since the adsorption uptake can be very sensitive to temperature and when comparing samples it is important to understand whether or not the comparative data were obtained under similar conditions. For certain applications, it may be prudent to incorporate temperature corrections into the data analysis (see Sect. 2.5).

2.4 Deactivation of sample with displacing agent

This step involves sample deactivation employing the displacing agent and measurement of volume of evolved test gas. The displacing agent represents a species that can, by modest volume, deactivate an adsorbent sample and release therefrom all of the test gas pre-adsorbed by carrying out step 2.2. Liquids are strongly preferred and for both convenience and efficacy, water is preferred for a broad range of adsorbents. The use of a precision glass syringe having "an easy to move" ground-glass syringe barrel with water as the displacing agent is particularly effective, since the water serves as a seal between the syringe barrel and the syringe body making the syringe effectively gas tight for collecting the displaced test gas. To begin the execution part of the test procedure, a known quantity of a suitable displacing agent, such as water is admitted into a syringe (see Fig. 2). The amount of displacing agent required is dictated by the sample amount used for the test and the quantity of displacing agent needed to fully deactivate that type of sample. The size of the

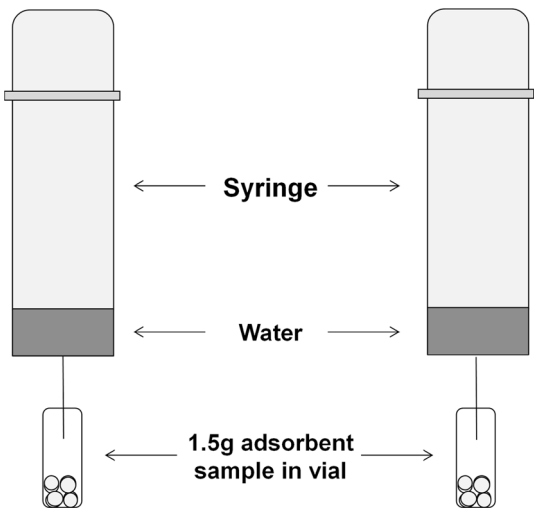

Fig. 2 Adsorbent pre-saturated in test gas and syringe filled with water displacing agent

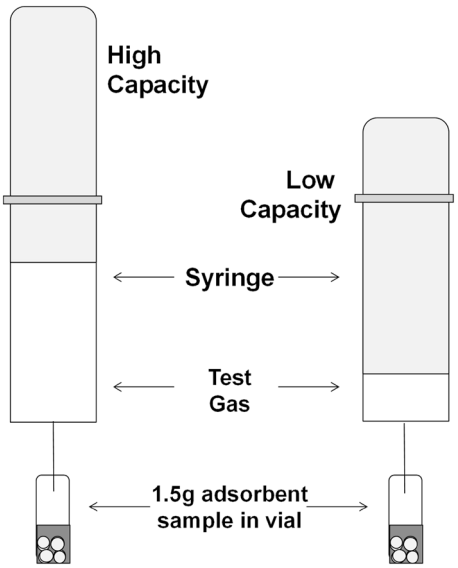

Fig. 3 Test gas release by displacing agent corresponding to high capacity and low capacity adsorbents

syringe selected for the test should have enough volume to house both the volume of displacing agent required for the test, as well as the amount of test gas expected to be released by the adsorbent sample. Essentially, there is no downside to using more displacing agent than the minimum required, provided that the syringe is sized sufficiently, since the objective is to fully deactivate the sample and recover all of the evolved test gas.

After the displacing agent is loaded into the syringe, it is injected into the sample vial through the septum, fully immersing the adsorbent sample and displacing the adsorbed test gas. During displacement, the adsorbent fully adsorbs the displacing agent thereby releasing all the adsorbed test gas. This displaced gas is then captured within the syringe barrel. In Fig. 3, this test gas capture is shown schematically for high and low capacity adsorbent samples.

2.5 Data analysis

One of the attractive features of this test method is that it is very visual in its nature. Adsorbents with high capacities will evolve larger amounts of test gas and vice versa for low capacity samples. From the extent of the movement of the syringe barrel upon deactivation of the sample with the displacing agent, a visual indication of the adsorption capacity of the sample is readily observable. The test can be made to be quantitative by using the recorded volume of test gas released and the initial sample weight to compute the volume of gas (ml) released per gram of sample. By comparison of the adsorption capacities, measured by the test for a series of samples from a plant or process with similar data for a known reference sample, any performance loss can be readily ascertained. The accuracy can be improved further by incorporating a weight correction to convert the as measured sample weight to an "unloaded" sample weight (see step 2.3) and a temperature correction to enable data recorded at different temperatures to be compared. This can be accomplished by measuring adsorption isotherms at different temperatures for the adsorbent of interest in order to derive a temperature correction factor. The capacity of the adsorbent for the test gas, obtained from this test method, can also be correlated with other parameters of interest. Useful correlations can involve relating the adsorbent capacity for the test gas to an amount of a contaminant of interest, which may be accumulating on the adsorbent sample over time. As a result of establishing such a correlation, the volume of test gas evolved can be converted to an estimate of the amount of contaminant present in the adsorbent sample. The determination of any decline in adsorption performance requires knowledge of the adsorption behavior of the specific adsorbent in use with the specific test gas in its fully activated and undamaged state. As an example of a useful correlation we and others have studied the capacity of Li–LSX as a function of residual moisture content (Hutson et al. 2000). A highly-exchanged fully activated Li–LSX sample adsorbs 25 ml/g of nitrogen at 27 °C and 760 Torr. Water contamination is a potential reason for the degradation of Li–LSX adsorbent performance in VPSA oxygen production systems. For a given adsorbent, test gas and conditions (temperature, pressure) a curve of test gas evolved per gram of sample versus % contaminant can be generated. For the Li–LSX adsorbent, curves of residual moisture content versus the capacity of the adsorbent for air are given in Fig. 4. These curves were generated by equilibrating the Li–LSX adsorbent sample with different amounts of moisture, measuring the residual moisture content of each sample using the Karl Fischer titration method and by recording adsorption isotherms on these variously contaminated samples at different temperatures. These data are reproduced in Fig. 4 where it can be seen how the capacity of the Li–LSX for air is decreased as the residual moisture content increases. These curves can be used in conjunction with the capacities of the Li–LSX for air, measured at a plant or process location using the test method described herein, to obtain an effective residual moisture content for the adsorbent in use.

3 Test method accuracy and validation study

In order to study the test accuracy, we undertook a reliability study with two operators running a series of ten tests, each using the same batch of sample. Isotherm data on the same sample were recorded for comparison. The isotherm data were recorded using a Micromeritics

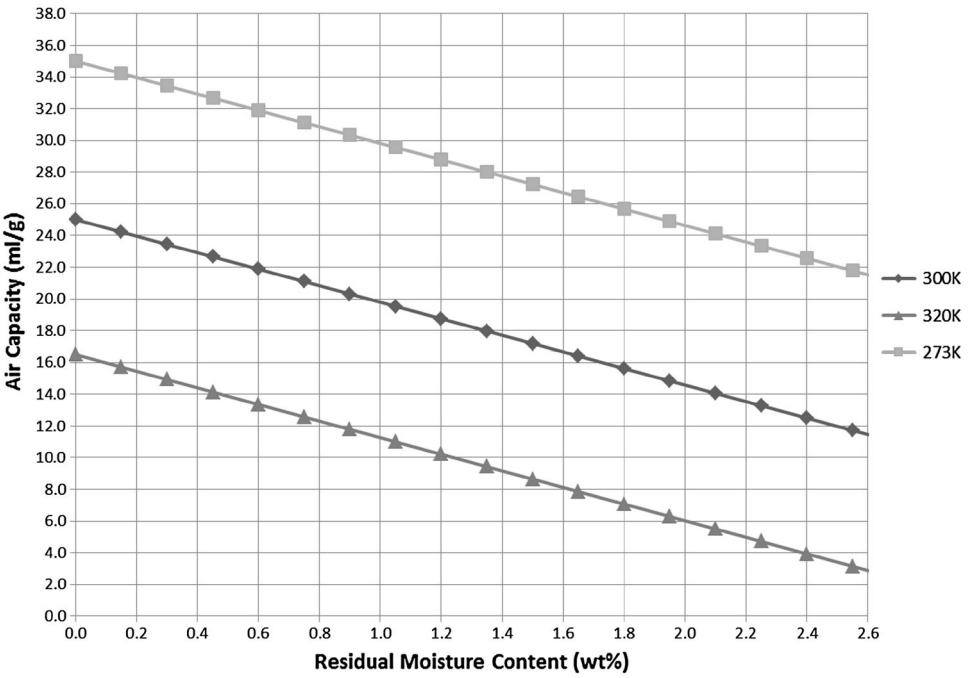

Fig. 4 The effect of residual moisture content on Li–LSX adsorbent capacity for air as a function of temperature

ASAP2050 extended pressure analyzer and an analytical grade balance with verified calibration was used to determine the sample weight. The sample chosen was a Li–LSX adsorbent with the test gas being nitrogen. The tests were run as follows: Each operator was provided with a 9 oz jar filled with enough of the Li–LSX adsorbent sample from the same batch of material for more than the intended ten tests. The samples were handled under a controlled atmosphere filled with dry nitrogen gas. Each test was started by having each operator weigh out ten sample vials of the Li–LSX adsorbent sample using an inexpensive balance with a digital scale reading to two decimal places. The motivation for the use of the inexpensive balance was that this test and method is designed for use in the field, at locations where analytical grade weighing balances are not expected to be available, meaning that a balance must be provided in the test kit that is small enough and robust enough to withstand transportation, as well as the non-ideal field environment. However, the lower precision of the inexpensive weighing balance will impact the test accuracy, since the intent is to express the measured gas volume released per gram of sample. The sample jar was opened under the dry nitrogen purge gas and loaded into a sample vial. The sample was exposed to the nitrogen purged controlled environment for a 60 s equilibration time, prior to the weight measurement. The 60 s equilibration time criteria was chosen based on experience with this Li–LSX sample. After each sample was weighed out, the sample weight was recorded and the sample vial sealed with its septa cap lid. A target sample weight of approximately 1.5 g was selected in view of the 22.4 ml/g nitrogen capacity determined for this Li–LSX sample using isotherm data at equivalent pressure and temperature. The temperature of the adsorbent was measured after saturation with nitrogen test gas and after the weighing process was completed and the average value during all of the tests was 26.6 °C. This entire process was completed a total of ten times by each operator. At this point, the sealed samples were removed from the nitrogen purged controlled environment in preparation for test execution using water as the displacing agent. A 50 ml syringe was chosen based on the expected adsorption capacity for this sample and sample mass weighed into each vial, as described above. In all tests, 4 ml of water was used as the displacing agent. The tests were executed one after the other, with the measured nitrogen capacity converted to the units of ml/g using the sample weight for each sample determined as described above. The results are shown without weight correction in Fig. 5a and with weight correction in Fig. 5b. The weight correction is applied using the method described in step 2.3 whereby the measured nitrogen capacities are converted from ml/g to wt% and the wt% value is used to calculate the weight of adsorbed nitrogen on the sample which is subtracted from the measured sample weight to yield an "unloaded" or "activated" sample weight.

With reference to Fig. 5a and b, it is clear that there is some variance in the measured N_2 capacities across the 10 tests from each operator. In the absence of the weight correction (Fig. 5a), 16 out of 20 data points fall below the N_2 capacity determined from the isotherm data on the same sample at an equivalent temperature and pressure. After the weight correction is applied in (Fig. 5b) the distribution of

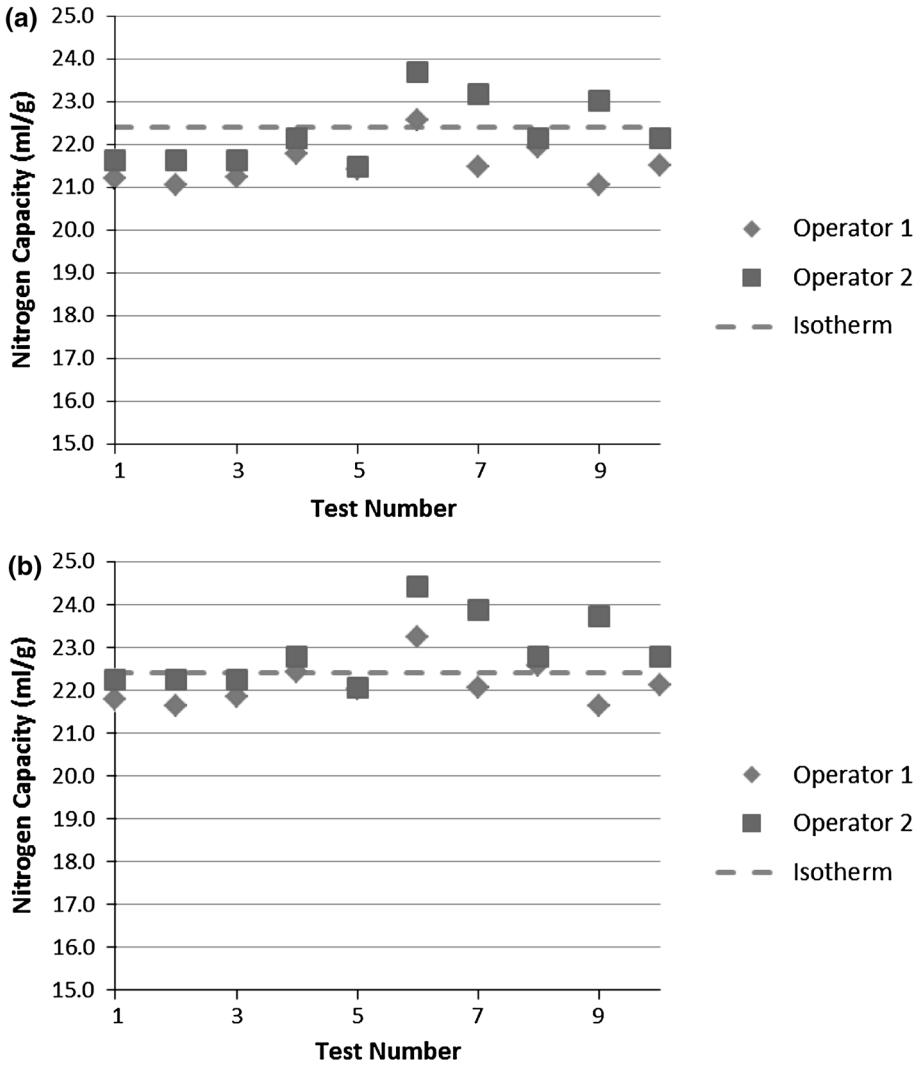

Fig. 5 Individual N_2 capacities **a** without weight correction and **b** with weight correction measured by Operator 1 and Operator 2 during the 10-test reproducibility study using a Li–LSX adsorbent. The capacity for the same sample at the equivalent temperature and pressure determined from isotherm data is also shown for comparison

data points is now more even with 11 data points below and 9 data points equal to or greater than the isotherm determined N_2 capacity. Sources of error in the test kit measured data can be from small losses of the displaced N_2 test gas through either the septa cap lid on the sample vial and/or through an imperfect liquid seal around the syringe barrel. The sample weight, determined by the comparatively low precision inexpensive weighing balance, represents another source of error and the static present inside the dry purged controlled environment in which the sample is handled, can make these weight measurements more difficult. Despite these test method limitations and imperfections, the measured adsorption capacity was never more than 1.3 ml/g away from the isotherm measured value with and without weight correction.

The results from a basic statistical analysis of these data are shown in Table 1. The data in Table 1 shows that mean N_2 capacity measured with and without weight correction is close to the isotherm determined value. The test is in fact accurate enough to measure nitrogen capacities on Li–LSX adsorbents to within ± 1 ml/g of the isotherm measured value, especially if a given test is repeated three times, which is our recommended practice. The use of the weight correction improved the test precision to ± 0.5 ml/g for the ten repeated measurements. Hence, if greater precision is required, running a larger number of repeats and using the weight correction is recommended. Once the test equipment is set-up, running repeat tests is very quick and not burdensome. The full test procedure for a given operator running ten repeat measurements took less than 1 h to complete. In general, a test accuracy of ± 1 ml/g is in fact very reasonable given the objective of providing a field test method and kit which is capable of rapidly diagnosing significant losses of adsorption capacity, where significant in this context equates to 15 % or more capacity loss, which at this level, could influence the ability of a commercial gas separation plant to perform as designed.

Table 1 Statistical data from the test method accuracy and validation study

Parameter (ml/g)	Non-weight corrected			Weight corrected		
	Operator 1	Operator 2	All data	Operator 1	Operator 2	All data
Mean	22.3	21.5	21.9	22.9	22.1	22.5
Median	22.2	21.5	21.6	22.8	22.0	22.2
Mode	21.6	21.1	21.6	22.2	21.6	22.2
SD	0.8	0.5	0.7	0.8	0.5	0.8

3.1 Case studies

In this section, two case studies are presented to show the utility of the test method and kit on two different classes of adsorbent with different test gases and displacing agents. In the first case study, we show an example from the field where the test method and kit were used to diagnose adsorbent performance issues with an Li–LSX adsorbent at a plant producing oxygen using VPSA technology. The Li–LSX adsorbent is hydrophilic and hence, water was used as the displacing agent and since its function is to adsorb nitrogen from air during the VPSA operation, N_2 was used as the test gas. In the second case study, an activated carbon adsorbent is tested to show that the test kit and method is not limited to hydrophilic zeolites and can be used for other classes of material. Due to the lower hydrophilicity of the activated carbon adsorbent, ethanol was selected as the displacing agent, in place of water. In addition, to showcase the use of a different test gas, CO_2 was used in place of N_2.

3.2 Case study 1: hydrophilic zeolite adsorbent using N_2 test gas and water displacing agent

Three samples of Li–LSX adsorbent were collected from a 2-bed axial VPSA plant where there was suspicion of adsorbent degradation which was contributing to performance loss. The Li–LSX adsorbent was an older generation product, compared to the sample used in the test method validation study, presented in Sect. 3 having an expected N_2 capacity of 19.5 ml/g. Two of the samples were taken from locations near the bottom of each of the two beds and a third sample was collected from the middle of one of the beds. Previous practice would have been to send these samples to a qualified third partly laboratory for a residual moisture content determination using the Karl Fischer titration method. Instead a kit containing all of the key equipment to perform the new test method had been sent to the plant site ahead of the sampling. This kit was employed to execute the test method described herein using dry N_2 as the test gas.

Table 2 Dataset from a VPSA air separation plant where the new test was used to diagnose adsorbent capacity loss

Bed	Bed A	Bed A	Bed B
Sample point	Bottom	Middle	Bottom
Sample weight (g)	1.50	1.71	1.50
Water added to syringe (ml)	4	4	4
Syringe reading after water injection (ml)	32	36	26
Volume of N_2 evolved from sample (ml)	28	32	22
N_2 capacity (ml/g)	18.7	18.7	14.7

The dry N_2 gas supply was used to purge out the glove bag and provide a suitable environment for sample handling. Each of the three VPSA plant samples was handled inside a glove bag to avoid any additional atmospheric contamination. The samples were equilibrated with the dry N_2 and 1.5–1.7 g of material was transferred to a sample vial containing a septum lid. The weight and temperature of each sample after equilibration with the dry N_2 was recorded. A 50 ml syringe was preloaded with 4 ml of water, as the displacing agent and in turn, the water was injected into each of the three sample vials to deactivate the sample and release the adsorbed N_2 gas. The volumes of water used and N_2 test gas released were recorded for each sample. The N_2 capacities for each sample were expressed per gram of adsorbent, without any weight correction. These test data are reproduced in Table 2.

From these data, it is apparent that the N_2 capacities of two samples from Bed A are equivalent and higher than the sample obtained from the bottom of Bed B. From a correlation of the N_2 capacity of Li–LSX to residual moisture content it was ascertained that the residual moisture content of the Li–LSX sample from the bottom of Bed B was approximately double that of the two samples from Bed A. These tests were completed in less than 30 min at the plant site and provided simple and intuitive results to support the plant remediation efforts.

3.3 Case study 2: activated carbon adsorbents using CO_2 test gas and ethanol displacing agent

Activated carbon adsorbents are used in a wide variety of industrial gas applications, including both purifications and bulk separations. A common purification usage of activated carbon is in H_2 PSA systems where one of the impurities that is often present and requires removal is CO_2. Hence, using CO_2 as the test for an activated carbon adsorbent from a H_2 PSA system would be a good indicator of performance in the application. Additionally, activated carbons in general have high CO_2 capacities under ambient pressure and temperature conditions which leads to measurable volumes of displaced test gas from small sample quantities. Furthermore, CO_2 availability at plant and field locations is generally good and small canisters manufactured for special cleaning applications are available and can be incorporated as part of the kit itself.

Given the lower hydrophilicity of most activated carbon samples, compared to low silica zeolites as tested above, it was necessary to identify an alternative displacing agent. Key features of the displacing agent are that it is strongly adsorbed by the adsorbent sample and capable of displacing the CO_2 test gas, has a small enough molecular size to access the same pores as the test gas, and furthermore it must also act as a seal to prevent the displaced CO_2 gas from escaping from the syringe used to collect and measure the volume of test gas released. The latter function is especially important, since the preferred syringes for the test are non-gas-tight varieties (gas-tight syringes are not preferred, since they offer too much resistance and can impede the collection and measurement of the volume of test gas displaced from a sample). In order to satisfy all these criteria, a liquid displacing agent is preferred with the added constraint that the liquid selected should be readily available and easy to handle. For the activated carbon testing, we selected ethanol as a good candidate for the displacing agent, which at first hand, meets all of the key criteria listed above.

Prior to any testing, the activated carbon samples were pretreated by heating in air at 150 °C and cooling down under dry N_2. Ten samples of the activated carbon adsorbent, denoted carbon 1, were weighed out into separate sample vials in a N_2 purged controlled atmosphere. Approximately 1 g of sample was weighed out and loaded into each sample vial, with the sample weight recorded for each of the ten samples. Note, the sample weight in this case study is the N_2 loaded sample weight, and no corrections were made to convert this to an "unloaded" sample weight. As in the previous case study, an inexpensive digital weighing scale was used as before for the sample mass determination. At this point, the ten sample vials were sealed with their septa cap lids and removed from the controlled atmosphere. Each sample in turn was then dosed with CO_2 test gas using the equipment shown in Fig. 1. A small CO_2 canister and regulator were purchased from Leland Industries and connected to a small flowmeter with scale 0–500 ml/min, the outlet of which was in turn, connected to a double needle, one used as an inlet and the other as an outlet. The double needle was inserted into the sample vial and a CO_2 purge of the sample was initiated at a flow rate of 100 ml/min. In each case, the flow of CO_2 was continued for 5 min. During this purge time, an infrared thermometer was used to monitor the sample temperature and ensure that this fell to a stable baseline value. After the 5 min equilibration time had elapsed, the flow of CO_2 was ended and then the double needle used for purging the sample was removed from the vial.

The expected adsorption capacity for activated carbon adsorbent, carbon 1, at equivalent temperature and

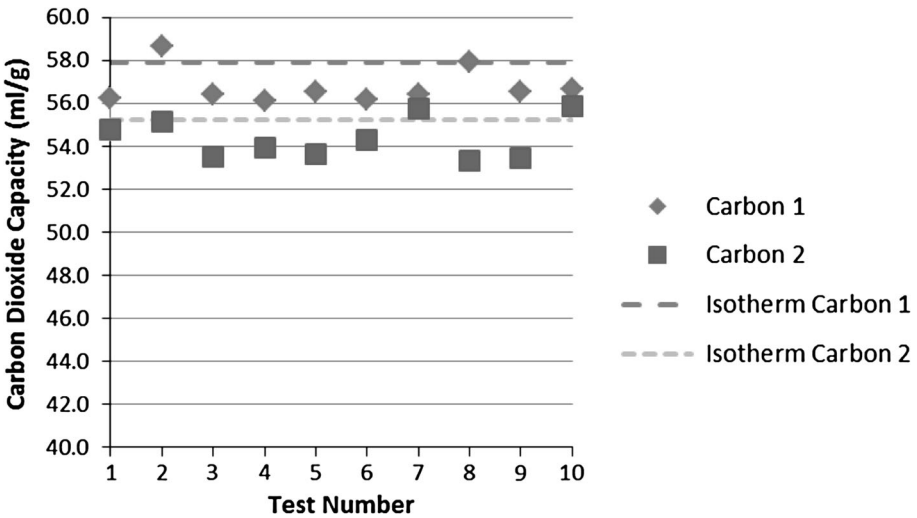

Fig. 6 Individual CO_2 capacities (non-weight corrected) measured on carbon 1 and carbon 2 during the 10-test reproducibility study using ethanol as the displacing agent. The capacity for the same activated carbon samples at the equivalent temperature and pressure determined from isotherm data is also shown for comparison

pressure, was determined from isotherm data recorded after vacuum activation of the sample at 150 °C, using a Micromeritics ASAP2050 extended pressure analyzer. The expected CO_2 capacity at equivalent temperature and pressure was 57.7 ml/g. As a result, a 100 ml syringe was used to ensure all of the evolved test gas from the $\sim$1 g sample could be captured and measured within the syringe. The CO_2 displacement was performed by injecting 5 ml of ethanol (ACS grade from Sigma-Aldrich) into the sample vial. This process of saturation of each sample with CO_2 and displacement with ethanol was repeated in turn for all ten activated carbon 1 samples. A second activated carbon sample, denoted carbon 2, with a slightly lower isotherm determined capacity of 55.2 ml/g was also tested using the procedure described above. The test kit CO_2 capacities for the carbon 1 and 2 samples are shown in Fig. 6.

With reference to Fig. 6, the test kit measured CO_2 capacities for the carbon 1 and 2 samples are generally lower than their respective isotherm values. This finding is consistent with the test results above for the validation study (see Sect. 3) using Li–LSX adsorbent, N_2 test gas and water as the displacing agent for the case without any sample weight correction. The higher volatility of ethanol compared to water may also decrease its ability to form an effective seal around the syringe barrel and possibly lead to additional losses of test gas during measurement. However, for both the carbon 1 and 2 test series, the test kit determined CO_2 capacity was not more than 1.8 ml/g away from the isotherm determined value and moreover, the test kit method is able to distinguish between these two carbon samples, despite the comparatively small difference in their CO_2 capacities. The mean CO_2 capacities from carbon 1 and 2 test series were 56.8 and 54.4 ml/g, respectively with the test kit data measuring a 4 % higher CO_2 capacity for carbon 1. The CO_2 capacities determined from the isotherm data for these two samples measured a 5 % higher CO_2 capacity for carbon 1 which is in excellent agreement with the test kit result. The standard deviations for the carbon 1 and carbon 2 series were 0.84 and 0.95 ml/g respectively which compares favorably with the values determined for the hydrophilic Li–LSX adsorbent presented in Sect. 3 which shows that the test method, as applied to a another adsorbent class using a different test gas and displacing agent is no less accurate than the validation case study. Overall, these results show that the test method is not limited to hydrophilic adsorbents, using water as the displacing agent, and can be used to study adsorbents with lower hydrophilicity, including widely used activated carbons. Moreover for activated carbons, the combination of CO_2 test gas and ethanol displacing agent yields CO_2 capacities that compare favorably with the isotherm measured values, at equivalent temperature and pressure.

4 Conclusion

In this paper, we have described a test method and associated equipment that can quickly and easily assess the performance level of adsorbents used in gas separation. We have explored the accuracy and reproducibility of the test itself on two different classes of adsorbent, namely a low silica zeolite and an activated carbon. In all of these cases, the test kit measured capacities were within 5 % of the values determined from isotherm data, at equivalent temperature and pressure. The test can be executed in the field and is particularly suited to diagnose whether adsorbents have been contaminated in a way that impacts their gas separation performance. The test method involves the determination of the gas capacity of an adsorbent using the principle of equilibrating the adsorbent with an appropriate test gas, deactivating the adsorbent and measuring the amount of test gas released. Due to the rapidity of the test method and simplicity of the test equipment, multiple samples can be analyzed directly in the field and a more complete picture of the extent of any adsorbent performance issues can be obtained. Moreover, the low cost of the test equipment and consumables, make it possible to carry out field evaluations of the adsorbent, as part of routine plant preventative maintenance. As a result, the signs of adsorbent degradation can be detected before it is too late and proactive measures to halt further loss of adsorption capacity can be implemented.

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