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A Proposed Surface Area Measurement Module for Rural Folks: Design Concept and Trial Setup

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A simple module for surface area measurement based on CO_2 adsorption at dry ice–methanol temperature was designed. The design consists of a sample tube, a glass syringe for pressure measurement, and an aspirator for evacuation. No sophisticated electronic device was used. Dry ice was used as a coolant in place of liquid nitrogen, which is widely used in ordinary BET surface area measurement. Vacuum tightness was confirmed acceptable when cooking oil was used as a seal liquid at the contact surface of the syringe. Error analyses were done for both vacuum tightness and the presence of residual gases due to the use of water-driven aspiration. Adsorption measurements of CO_2 were conducted using the simple module and a conventional apparatus. Results confirmed that the module works well within reasonable experimental error, if the weight of sample and the initial intake of sample gas are chosen properly. However, since the adsorption isotherms of several carbon samples showed a plateau at high pressure, the BET equation was not applicable. Instead, the Langmuir one-point methodwould be recommended for surface area measurement.

Keywords: Adsorption isotherms, BET (Brunauer-Emmet-Teller) equation, charcoal, CO_2 adsorption, Langmuir equation, *and* simple module.

INTRODUCTION

Water contamination is a perennial problem in developing countries because water supply systems are neither well provided nor evenly distributed throughout rural areas. Thus, the researchers propose to design a water-treatment module that can be set up by assembling items that are available to local peoples.

Wood charcoal, produced by traditional method, can be used as an adsorbent for water contaminant if it is activated using an appropriate procedure. The properties of charcoal may differ from one batch to another; therefore, the properties of charcoal need to be examined in order to convince people to use it. *Surface area* is one of the parameters for quality assurance. Despite the availability of commercial equipments, they are very expensive and much complicated for use by ordinary rural folks or even by local health officers.

The objective of this study is to design and manufacture a simple module for surface area measurement. The criteria behind the design of this module are: (a) simple operation, (b) availability of chemicals to be used in the measurements, and (c) low price with an acceptable performance.

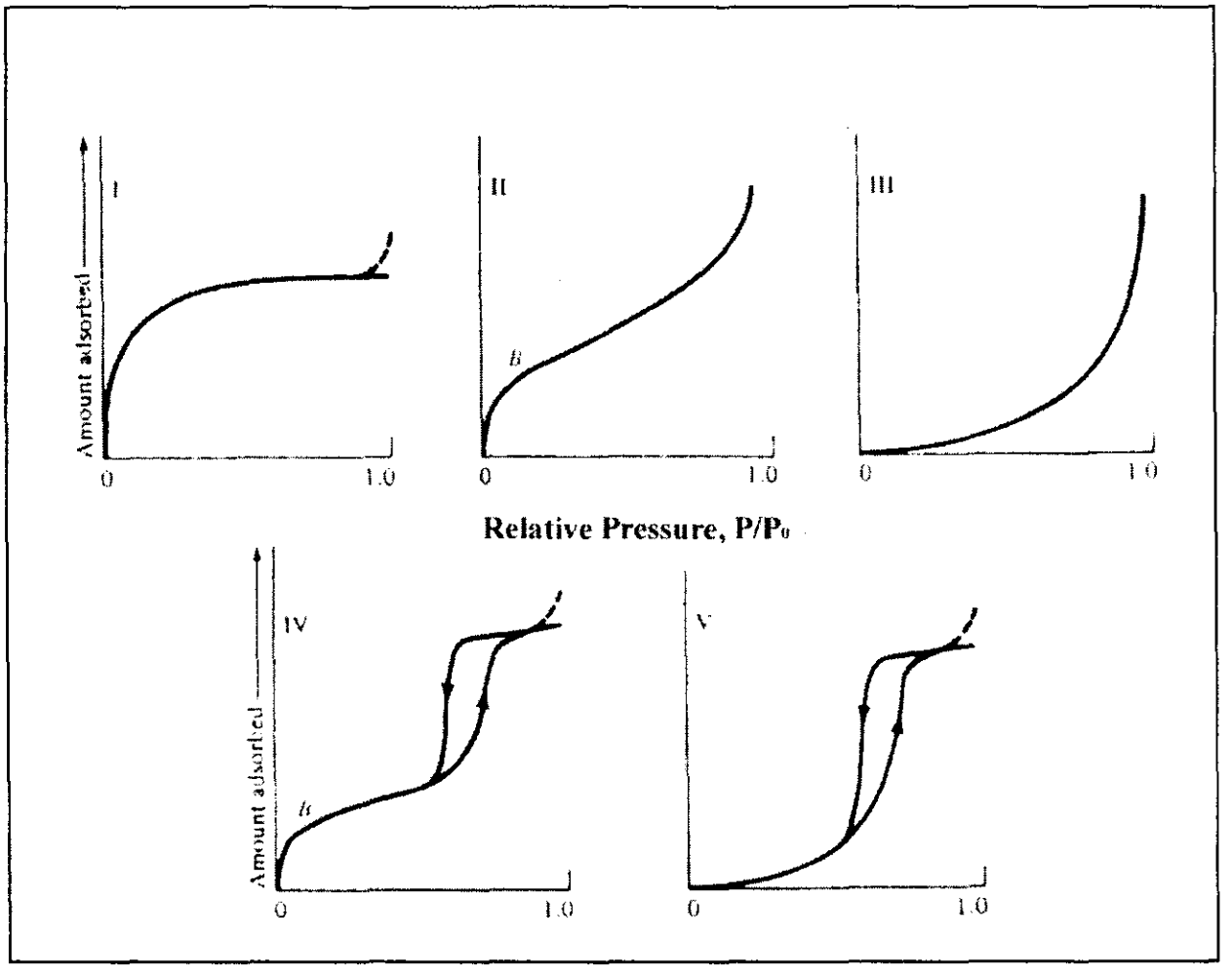


Figure 1. The Five Types of Adsorption Isotherms (As classified by Brunauer et al. 1940)

The fundamental principle for measuring surface area of porous material is to analyze the adsorption isotherm of a particular adsorbate onto the surface. The physical adsorption isotherms have been classified by Brunauer et al. (1940) into what is generally known as the *BDDT classification* (see Figure 1). In any case, the adsorption amounts increase steeply at the highest pressure range by multilayer adsorption. The point of monolayer adsorption is very clear in some isotherms, but is either not clear or not found in other cases. The researchers, therefore, used multi-points measurement to fit to the theoretical curve, in which n_m is included as a parameter. This curve fitting gives n_m, which yields surface area in due course.

In the conventional procedure, nitrogen is widely used as an adsorbate at liquid nitrogen temperature (77 K), although any condensable inert vapor can be used at any temperature theoretically (Satterfield 1993). Practically, however, several other factors have to be considered in choosing an adsorbate and a coolant as in this present study. The first is safety. The adsorbate should be nontoxic and nonexplosive. The second is affordability. The adsorbate should be easily available at a low price.

CO_2 adsorption at dry ice–methanol temperature (195 K) was chosen because dry ice was thought to be easily available even in rural areas, such as from ice cream shops. Experimentally, the measurement at P/Ps = 0.05–0.3 was recommended for BET equation. Accuracy of the measurement is higher when absolute pressure, *P*, is high. Therefore, for ordinary BET measurements, the adsorption of a gas at the gas liquefaction temperature is preferably used, so that *P* equals to P/Ps (*Ps* = 1 atm at the temperature).

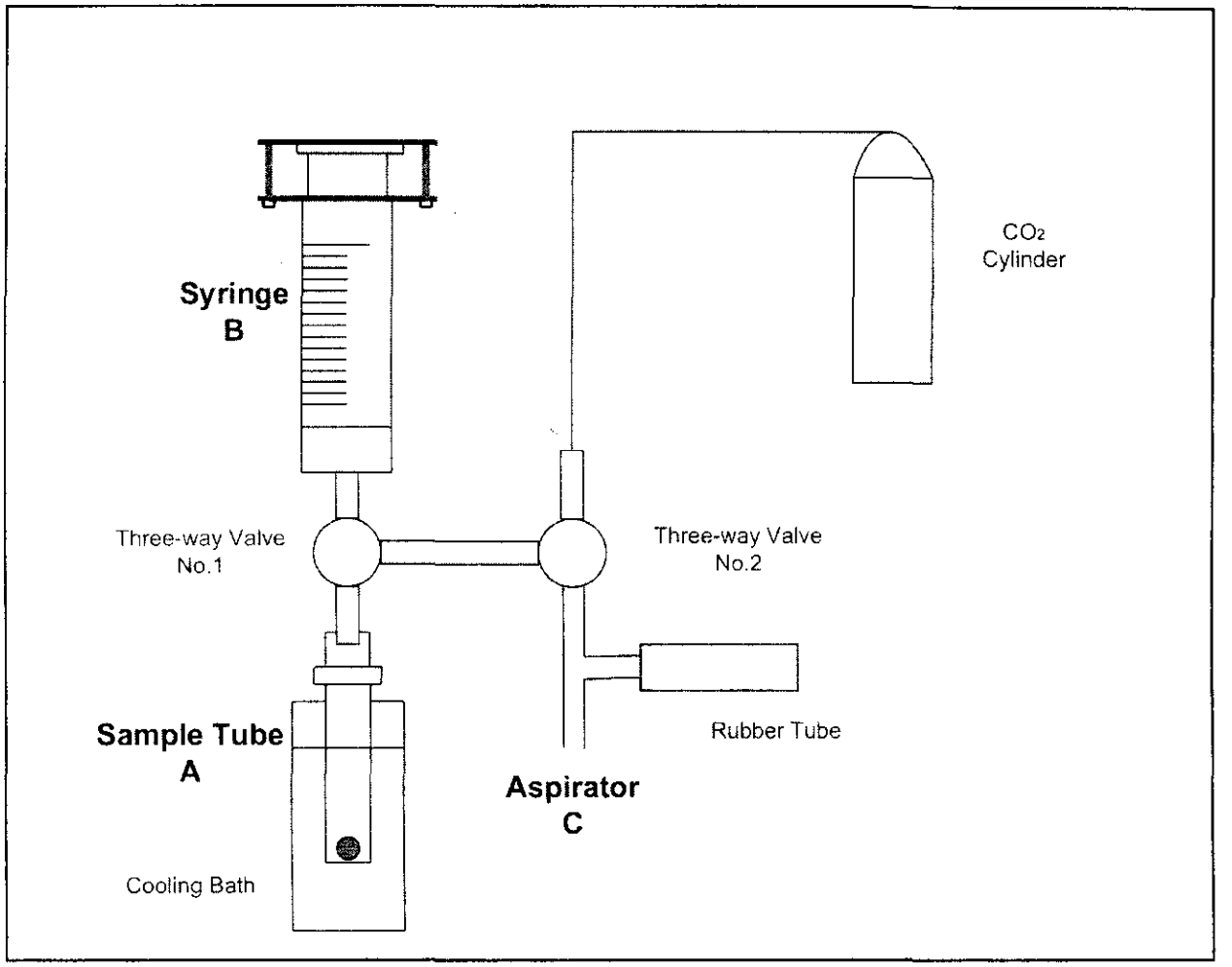


Figure 2. The Schematic Drawing of Simple Surface Area Measurement Module

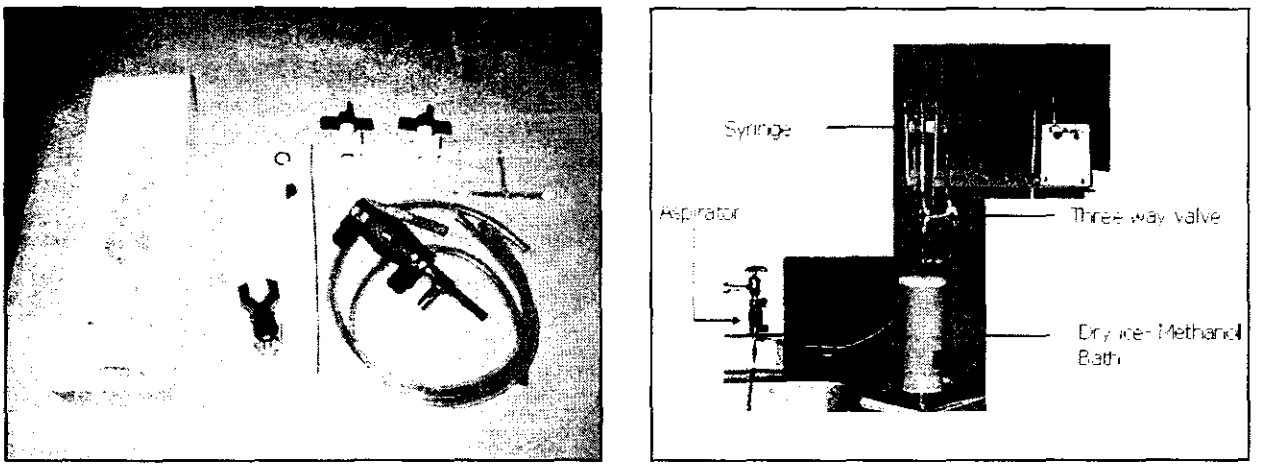
Gonzalez-Vilchez et al. (1979), Rodriguez-Reinso et al. (1982), Nakashima et al. (1995), and Della Rocca et al. (1999) studied CO_2 adsorption at 273 or 298 K. Adsorbed amounts of CO_2 at these temperatures are quite small, therefore, the accuracy of measurement becomes poor. For the present purpose, high accuracy cannot be expected from small amounts of adsorption. Therefore, CO_2 adsorption at dry ice–methanol temperature was chosen.

EXPERIMENTAL

Four samples were used in this study. Activated carbon of commercial grade was obtained from Wako Pure Chemical Industries. Activated charcoal was prepared by treating commercially available charcoal in a handmade furnace under water vapor. Two other kinds of charcoals were used (one was purchased from a supermarket in Thailand, one produced from bamboo which came from Japan) in the adsorption studies.

The module is illustrated in Figure 2 (for photos of the parts and the actual setup, see Figure 3). The module's essential parts are: sample tube A for placing the sample, syringe B for measuring pressure, and aspirator C for evacuating the system.

During the adsorption, the sample tube was immersed in a coolant bath of dry ice–methanol. The samples were ovendried at 383 K overnight and stored in a desiccator. The weighed sample was placed in the sample tube, outgassed for 15 min, and then isolated by closing valve 1. One atmosphere of CO_2 was introduced to the syringe, and the initial volume, V_0 was recorded. The inner piston was fixed by a cramp at the position of balance under one atmosphere. The sample was



(a) (b)

Figure 3. Photos of the Simple Surface Area Measurement Module: (a) Important Parts and the (b) Actual Setup

$$n = \frac{1}{R * T}\left(V_0 - \frac{V_0'}{V_0} * (V_0 + V')\right) \qquad (1)$$

Where, V_0 is initial intake volume of syringe B, V_0 is final volume, and V is the corrected volume due to nonisothermal temperature of the sample tube, equals to 18 ml.

In some cases, lower initial pressure of CO_2 was applied by pulling up the inner piston after one atmosphere of CO_2 was introduced. Equation 1 was modified appropriately to suit the case.

The adsorption isotherm of CO_2 on activated charcoal at 195 K was also determined in a conventional volumetric system to compare with the performance of the simple module. The sample was outgassed at 523 K for 2 h under vacuum before the adsorption measurement. The volume of gas adsorbed was determined as a function of gas pressure from 2 to 70 kPa. When the pressure change ceased to occur for about 5 min, the adsorption was considered to be in equilibrium.

RESULTS AND DISCUSSION

Part I: Performance Test

Leak and Friction Test

The syringe was used as a gas container of fixed volume during the adsorption and of variable volume room for measuring equilibrium pressure. Cooking oil was used as seal liquid at the contact surface of the inner piston and the outside wall. In order to assure vacuum tightness, the test was conducted at high pressure (190 kPa) and low pressure (1.9 kPa): the syringe was pressurized or evacuated while the inner piston was fixed by a cramp. The leakage was beyond detection, as evidenced when the original volume reading value was restored after the piston was released.

Whether or not the friction of the piston affects the measurement was also tested. If the friction is great, the piston may stop at a point where exact pressure balance was not established. After the stop, the researchers repeated the push-and-release and pull-and-release procedures for the inner piston. Likewise, the piston moved back to the same position, which showed the position is under the exact balance.

Pressure and Volume Correction

It was observed from the force balance consideration that the inner pressure did not equal to the outer pressure when the piston was freed from the cramp. Additional pressure due to the weight of the piston should be considered; however, since it was estimated to be less than 0.36 kPa, it could be safely neglected.

Since a part of the sample tube is immersed in the coolant bath while other part is above the coolant surface at an unidentified temperature, the volume accommodated more amount of gas than was calculated from the true volume at room

temperature. The researchers measured experimentally the correction factor in terms of "corrected volume."

Performance of Aspirator

Water-driven aspirator was used as evacuation pump. The flow rate of water may affect the performance of aspirator. It was found, however, that residual pressure was constant at 1.9 kPa while the water flow rate remained higher than 5 ml/min. This pressure is consistent with the vapor pressure of water at room temperature. The aspirator can evacuate the system but not lower than the value of water vapor pressure at the ejection point.

Effect of Remaining Gas on the Adsorption Data

As mentioned earlier, some gas remained which affect the adsorption measurement. It could be reasonably assumed that the remaining gas is either air, water, or a mixture of the two.

On the one hand, if the remaining gas is water, water would be kept on the surface in the form of ice crystal when the adsorption run is conducted. Therefore, water would not affect the pressure at equilibrium. However, this would result in smaller CO_2 intake than was calculated from the volume–pressure data. On the other hand, if the remaining gas is air, they

Table 1. Percent Deviation of Uncorrected Data vs. Corrected Data Due to Residue Gases

Data from Simple Module	Surface Area *(Langmuir Eq.)* (m^2/g)	% Deviation
Uncorrected Data	436.72	—
Corrected Data		
with air as a residue gas	431.79	1.14
–with water as a residue gas	430.69	1.38
–with 50% air and 50% water as a mixed residue gas	431.28	1.26

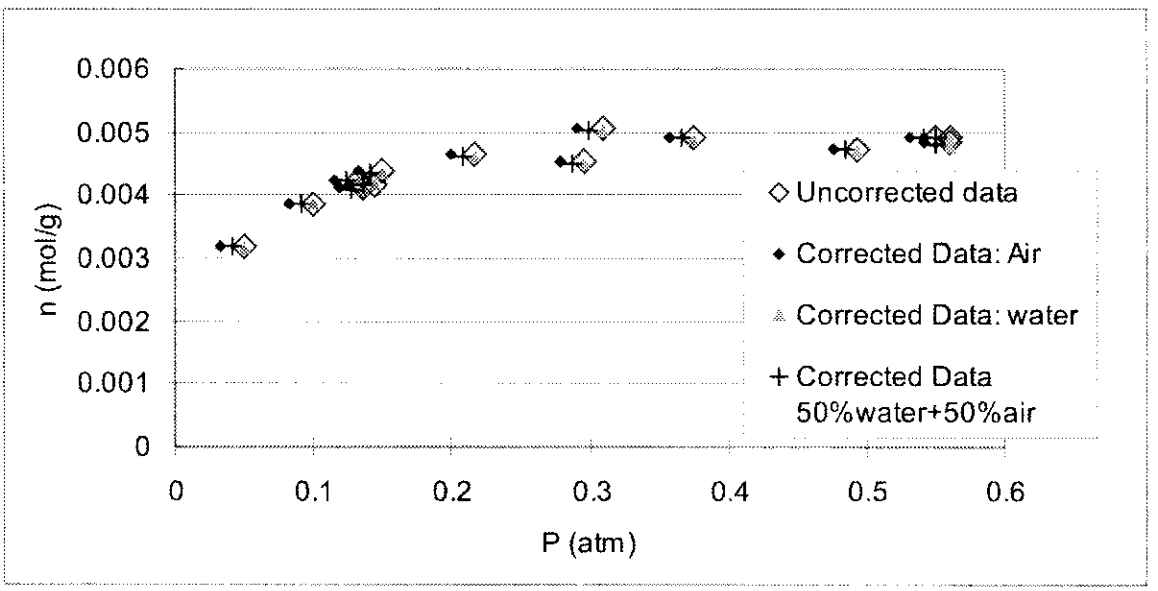


Figure 4. Effect of Remaining Gas on Adsorption Isotherm of CO_2 on Activated Charcoal at -78°C

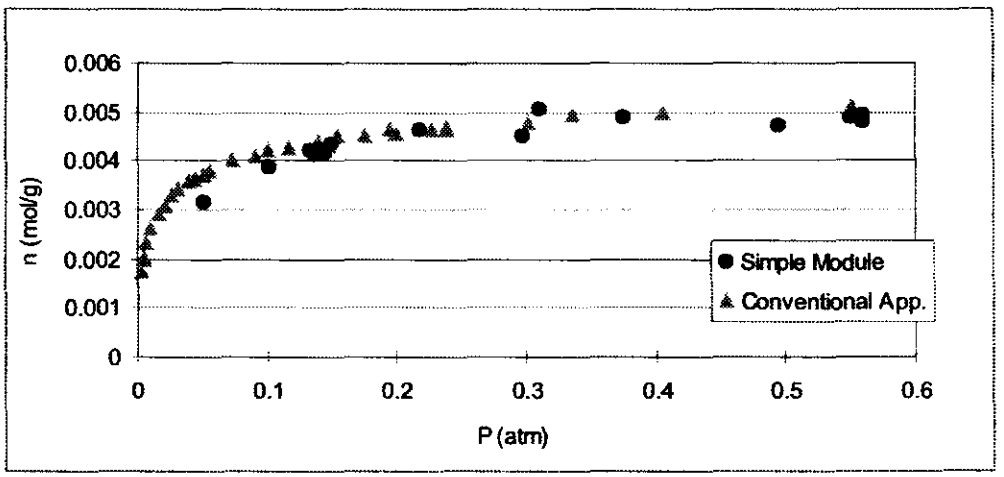


Figure 5. Comparison of Adsorption Isotherms (Simple Module vs. Conventional Adsorption Apparatus)

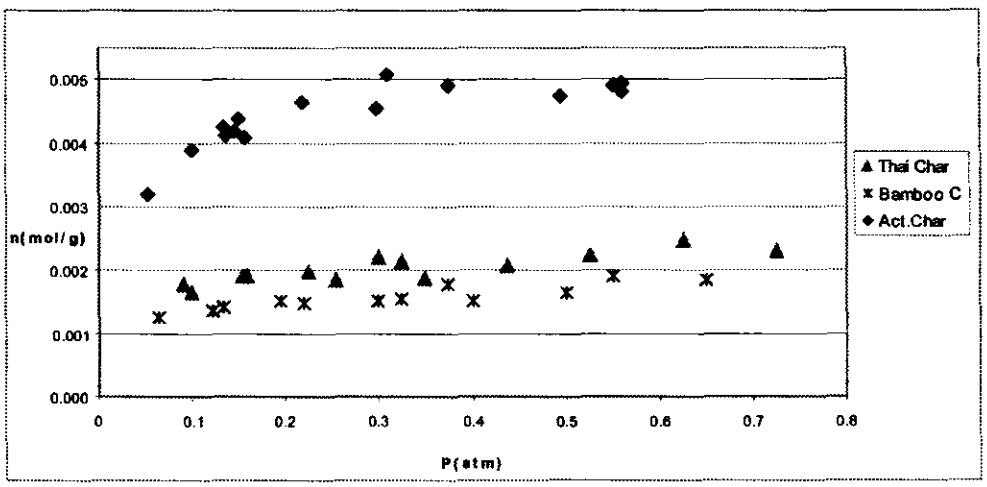


Figure 6. Adsorption Isotherms of CO_2 on Thai Charcoal, Bamboo Charcoal, and Activated Charcoal at Dry Ice–Methanol Temperature, -78°C (Measurements Are Done by the Simple Module)

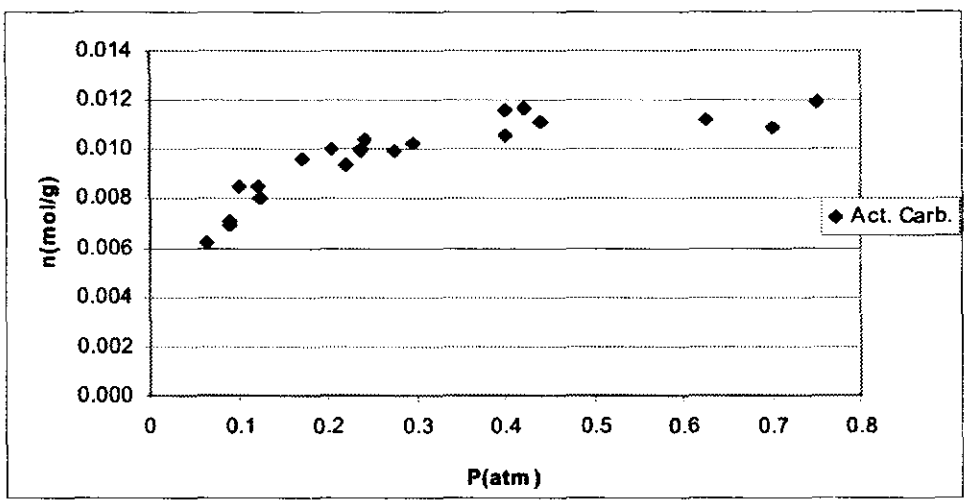


Figure 7. Adsorption Isotherms of CO_2 on Activated Carbon at Dry Ice–Methanol Temperature, -78°C (Measurements Were Done Using the Simple Module)

(N_2 and O_2) will remain in the gas phase during the adsorption. The calculated pressure was not the pressure of CO_2 alone but the sum of CO_2 and air.

The aforementioned effects may be summarized as follows: If one assumes that the remaining gas is water, the error will occur on the amount of adsorption; however, if the gas is air, the error will be on the equilibrium pressure. In the case that the remaining gas is a mixture of water and air, the error will occur both on adsorbed amount and the pressure at equilibrium.

The results of the uncorrected and corrected data with the three assumptions above are given both in Figure 4 and in Table 1. In Table 1, the Langmuir equation was used to determine surface area. The surface area without correction with residue gases gave an overestimation in the range of 1.14–1.38%. Note that when the BET equation was applied, the effect of the two gases turned out the opposite: If two gases coexist, the error cancels out. Therefore, one may conclude that the correction is not very important. Thus, in the succeeding figures, such corrections are no longer applied.

Comparison of Adsorption Isotherms with Conventional Apparatus

The adsorption isotherms of activated charcoal as measured using the simple module and the conventional adsorption apparatus are compared in Figure 5. The data, however, showed very small difference, especially at lower pressure. This is due to the effect of remaining gas in the system that becomes important at the lower pressure. At high equilibrium pressure, the adsorption amount measured by the two methods lies within general scattering of the points. It could, therefore, be concluded that the simple module showed a good performance for adsorption measurement; that is, with the purpose limited to measuring the saturation point.

Part II: Adsorption Isotherm and Surface Area Measurement

The adsorption isotherms of CO_2 on carbon-based adsorbent are illustrated in figures 6 and 7. Adsorption data were analyzed by Langmuir and BET equations to determine monolayer amount and surface area. All the parameters (n_m, K, and C) and surface areas from both equations are listed in Table1.

All the adsorption isotherms are of type I, with plateaus for quite a wide pressure range, 0.2–0.7. Therefore, it would be better to use the Langmuir equation in determining monolayer capacity rather than to the BET equation. Moreover, the value of C given in Table 1, which is a constant related to the heat of adsorption and the liquefaction of gas, is negative for both charcoal and activated charcoal. Everette et al. (1974) found the negative value of C for several kinds of carbon black and suggested that it might have arisen from the inadequacy

Table 2. Parameter Constants and Surface Areas from the Langmuir and BET Equations

Sample	Langmuir Equation			BET Equation		
	n_m *(mol/g)*	K *(atm^{-1})*	Surface Area *(m^2/g)*	n_m *(mol/g)*	C	Surface Area *(m^2/g)*
Activated Carbon	0.012450	17.04	1057.73	0.007799	79.95	662.32
Sample 1	0.005160	32.39	436.72	0.003360	-150.69	285.56
Sample 2	0.002509	16.96	213.07	0.001308	-36.18	111.08
Sample 3	0.001965	15.83	166.93	0.001027	-48.16	87.19

Notes:
Sample 1. Activated charcoal using charcoal made of wood available in the Japanese market.
Sample 2. Charcoal purchased in a supermarket in Thailand.
Sample 3. Charcoal made of bamboo and obtained from a Japanese NPO.

of the BET theory. They recommended the use of the Langmuir equation rather than the BET equation for porous carbon samples.

Langmuir isotherms held well for all the samples tested. If the measurement was done at plateau region, the adsorbed amount would directly give the surface area: hence, the Langmuir one-point method wold be applicable. Thus, the researchers recommend an equilibrium pressure higher than 40 kPa (0.4 atm) for the evaluation of surface area. The data points scatter but to ±10% from the fitted line.

CONCLUSIONS

A simple handmade module for surface area measurement was designed. The module, which would cost US$100, was not equipped with any electronic and/or electric device. Dry ice was used as a coolant instead of liquid nitrogen. All the items and chemicals that the module would need were within reach of rural folks in developing countries.

The researchers suggest the module for use by local health centers in rural areas, especially where water contamination is a serious problem, to assure the quality of charcoal or activated charcoal for in-house water treatment.

CO_2 adsorption at dry ice temperature onto various carbon samples was conducted in order to confirm the soundness of the module. The isotherms obtained using the module were in good coincidence with those obtained using a conventional well-equipped adsorption apparatus that is vacuum-tight, glass-made, and equipped with electric and/or electronic devices. Since the coincidence was noted to be better at the higher pressure region, the BET or Langmuir one-point method would be applicable.

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