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Saturday, December 25, 2010
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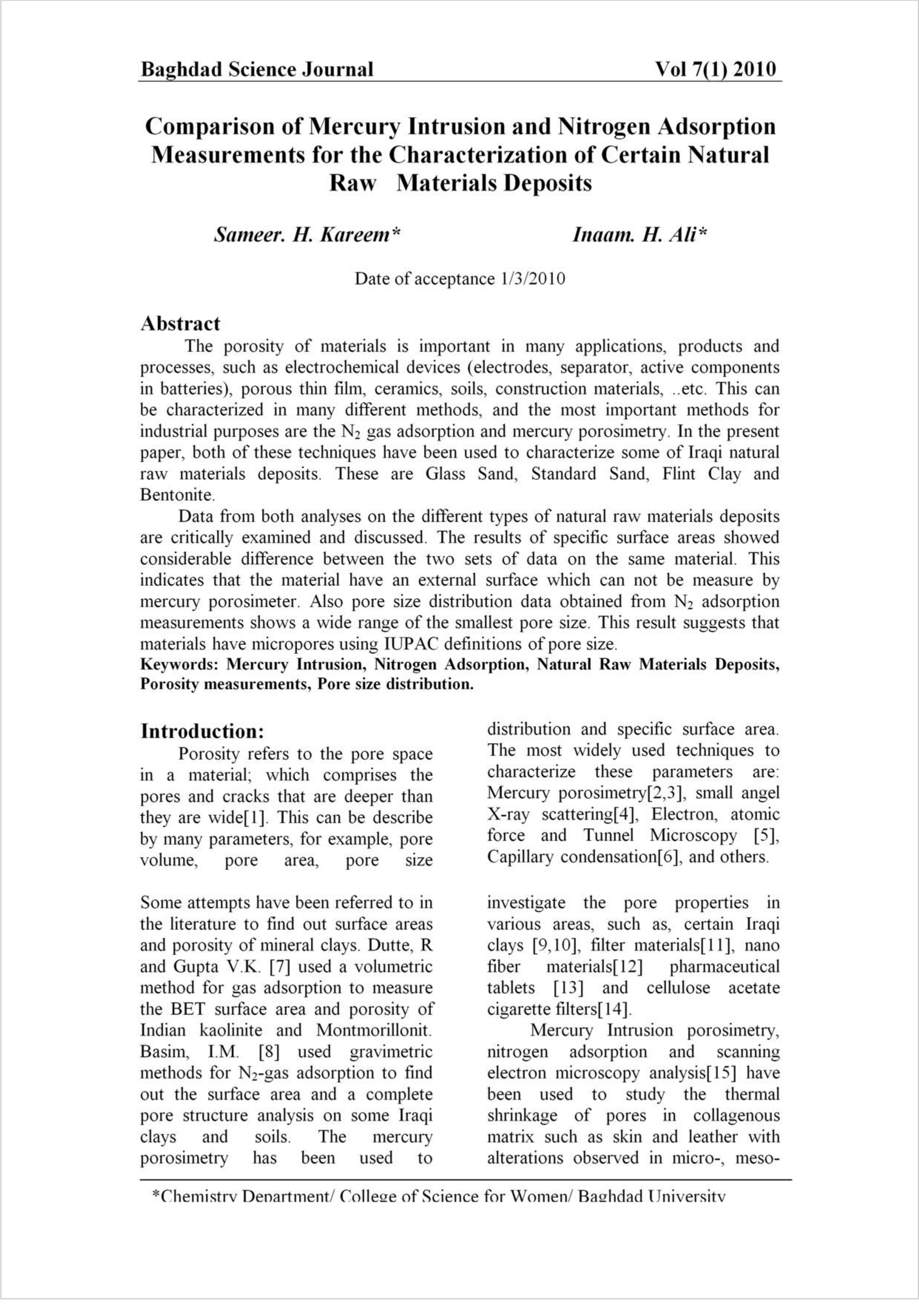

Baghdad Science Journal **Vol 7(1) 2010**

Comparison of Mercury Intrusion and Nitrogen Adsorption Measurements for the Characterization of Certain Natural Raw Materials Deposits

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Date of acceptance 1/3/2010

Abstract

The porosity of materials is important in many applications, products and processes, such as electrochemical devices (electrodes, separator, active components in batteries), porous thin film, ceramics, soils, construction materials, ..etc. This can be characterized in many different methods, and the most important methods for industrial purposes are the N_2 gas adsorption and mercury porosimetry. In the present paper, both of these techniques have been used to characterize some of Iraqi natural raw materials deposits. These are Glass Sand, Standard Sand, Flint Clay and Bentonite.

Data from both analyses on the different types of natural raw materials deposits are critically examined and discussed. The results of specific surface areas showed considerable difference between the two sets of data on the same material. This indicates that the material have an external surface which can not be measure by mercury porosimeter. Also pore size distribution data obtained from N_2 adsorption measurements shows a wide range of the smallest pore size. This result suggests that materials have micropores using IUPAC definitions of pore size.

Keywords: Mercury Intrusion, Nitrogen Adsorption, Natural Raw Materials Deposits, Porosity measurements, Pore size distribution.

Introduction:

Porosity refers to the pore space in a material; which comprises the pores and cracks that are deeper than they are wide[1]. This can be describe by many parameters, for example, pore volume, pore area, pore size distribution and specific surface area. The most widely used techniques to characterize these parameters are: Mercury porosimetry[2,3], small angel X-ray scattering[4], Electron, atomic force and Tunnel Microscopy [5], Capillary condensation[6], and others.

Some attempts have been referred to in the literature to find out surface areas and porosity of mineral clays. Dutte, R and Gupta V.K. [7] used a volumetric method for gas adsorption to measure the BET surface area and porosity of Indian kaolinite and Montmorillonit. Basim, I.M. [8] used gravimetric methods for N_2-gas adsorption to find out the surface area and a complete pore structure analysis on some Iraqi clays and soils. The mercury porosimetry has been used to investigate the pore properties in various areas, such as, certain Iraqi clays [9,10], filter materials[11], nano fiber materials[12] pharmaceutical tablets [13] and cellulose acetate cigarette filters[14].

Mercury Intrusion porosimetry, nitrogen adsorption and scanning electron microscopy analysis[15] have been used to study the thermal shrinkage of pores in collagenous matrix such as skin and leather with alterations observed in micro-, meso-

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and macroporic structures, and a comparison of results obtained has been made. Occelli M.L et al [16] reported a method for determination of pore size distribution, surface area, and acidity from theoretical models of adsorption and from microcalorimetry methods. The method was based on nonlocal density functional theory (NLDFT) and used to interpret the data for the adsorption of nitrogen at 77K within the pores of three different commercial Zeolite-based fluid cracking catalyst before and after their use in a refinery catalytic cracking unit. Three methods [17], mercury intrusion porosimetry, NMR cryopometry and DSC thermoporosimetry, have been compared in Characterizing pore size distributions of compressed finely samples. Galarneau A. et al [19] reported that the mesoporous silicas (MCM-41 and SBA-15) have a size range (3-10 nm diameter) represented an ideal tested to compare the performance of nitrogen adsorption and mercury porosimetry techniques. In this investigation, both the mercury ground calcium carbonate tablets which is compacted to five different porosity levels. The comparison between the three methods were performed by observing the respective reported pore volume of the samples, taken within a relevant pore diameter range, together with the respective pore sizes distribution that the three methods gave.

Gane P.A.C. et al [18] used three different measurement techniques to characterize five samples of fine particles size calcium carbonate, typically used as excipient or as active pharma ingredient. These methods are mercury porosimetry, hexadecane imbibition and hexadecane permeability, which have been used to establish the pore size distribution within the packed structures of porosimetry and N_2- gas adsorption techniques have been used to characterize some Iraqi mineral raw materials and the results obtained for surface area, pore volume and pore size distribution have critically compared.

Experimental

Materials

The natural mineral raw materials as glass sand, standard sand, flint clay and bentonite were used in this research, which have been obtained from state company of geological survey and mining- Ministry of Industry and Minerals- Iraq. The specification of glass sand, flint clay and bentonite are presented in table (1), while the standard sand is processed (washed and sieved) sand used for cement testing. It constitutes about 10% of the total sands of Al-Hussainiya formation and the SiO_2 content is 98% [20]. The samples were ground and sieved and the powder that's the particle size between 106 and 202 µm has been used.

Table (1): Chemical composition of different natural minerals

Type	Chemical Analysis								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	L.O.I
Glass sand	96.5-98	0.5-1.6	0.3-0.5	0.1-0.2	0.1-0.4	0.1-0.2	< 0.1	< 0.1	-----
Flint clay	38-45	35.5-41.5	0.5-1.96	1.4-3	0.2	0.1	--------	-------	13.4-15.1
Bentonite	56.7	15.7	5.12	---------	4.5	3.4	1.1	0.6	9.5

Apparatus:

The measurements were made using:

1- Micrometrics Gemini 2360 analyzer with a selectable calculation of the following: single point, BET multipoint surface area and total pore volume. This measurement is done in Cardiff university- school of chemistry laboratories.

2- Mercury porosimetry model "pore size 9320" obtained from micromeritics, USA. This instrument characterizes the pores ranging from 0.006 mm to 360 mm and capable of generating pressures ranging from 0 to 30.000 psi. This measurement is done in the laboratories of Ibn-Sina State Company- Baghdad.

Technique

1- N_2-gas adsorption

In the volumetric method, the apparatus is evacuated and heated until the specimen is adequately degassed. After the degassing process, the sample is held at a constant temperature, usually near or at the boiling point of the adsorptive. The adsorptive pressure is increased step-wise and held constant for a period of time to allow the adsorption to occur. The amount adsorbed is measure by measuring the pressure change and comparing this to the expected pressure change if the adsorbed were absent. The measurements proceed automatically recording the adsorption isotherm in about 20 steps from vacuum (10^{-6} torr) up to atmospheric pressure, followed by recording the desorption isotherm also in a bout 20 steps back down to vacuum.

2- Mercury porosimetry:

In this technique, the gas is evacuated from the sample cell, and mercury is then transferred into the sample cell under vacuum. Mercury is non-wetting to the sample; therefore, it does not flow into the pores of the sample. On increase of pressure on mercury, it flows into the pores and the pressures required for intrusion of mercury into a pore of diameter D is given by the following relation [21] : $D = -4 \gamma \cos \Theta / p$

Where D is the diameter of the pore assuming the pore to be cylindrical, p is the differential pressure, γ is the surface tension of mercury taken as 0.485 N/m and Θ is the contact angle taken as 140. Accurate measurement of pressure and volume of intrusion yields pore size and pore volume distribution.

Results and Discussion:

Nitrogen gas Adsorption

The adsorption-desorption isotherms of nitrogen at 77K on the four types of the deposits have been constructed by plotting the volumes of nitrogen adsorbed at 77 K on the specimen against the corresponding relative pressures (P/P_o). The isotherms obtained are shown in fig (1).

The isotherms of fig (1) are classified as type IV according to BET classification [22]. and the isotherms of bentonite, glass sand and standard sand have a type "B" hysteresis loop according to de Boer's classification, while the isotherm of flint clay has a type "A" hysteresis loop. These hysteresis loop indicates the pore structure has a uniform cylindrical form with no evidence of "ink bottle" pores for flint clay, while the other samples bentonite, glass sand, and standard sand have a pore structure type slit-shape.

The surface area of the four types of natural deposits have been calculated from isotherms using two methods:-

1- Single point: In this method, the volume of monolayer is calculated at $P/P_o = 0.2979$.

2- BET method : In this method, the monolayer capacity is calculated according to the BET equation[23]

$$\frac{P}{V\,(P_o-P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC}\;\frac{P}{P_o} \quad \ldots\ldots\ldots (1)$$

Where V is volume adsorbed, V_m volume of monolayer, P sample pressure, P_o saturation pressure, and C constant related to the enthalpy of adsorption (called BET constant). By plotting the quantity on the left of equation (1) versus P/P_o one can add the slope and intercept of this plot to obtain V_m. The plot should be taken over the 0.05-0.35 P/P_o range. A typical plot for bentonite deposits is shown in fig (2).

$$\text{Slope(s)} = \frac{C-1}{CV_m} \quad ; \quad \text{Intercept (I)} = \frac{1}{CV_m}$$

From the above equation, the $V_m = \dfrac{1}{S + I}$

The specific surface area (Ss) is then calculated from V_m by the following equation:-

$$S_s = \frac{V_m\,N\,a_m}{22414\ m} \quad \ldots\ldots\ldots\ldots (2)$$

Where N is Avogadro number, a_m the cross sectional area occupied by each nitrogen molecule (0.162 nm^2), and m weight of the sample. Table (2) presents the values of specific surface area for the four deposits.

Table (2): The specific surface area of the four types of raw materials deposits

method	Raw materials deposits			
	Bentonite	Glass sand	Flint clay	Standard sand
Single point	310.40	230.41	272.93	279.31
BET m^2/g	317.55	241.87	278.96	287.03

The total pore volume has been determined also by two methods, the single point method at $P/P_o = 0.9923$ and the method of Barrett, Joyner and Halende[24] (BJH) adsorption cumulative volume of pores. In this procedure the Kelvin equation is used to calculate the radius r_p of the capillaries, which are assumed to be cylindrical:-

$$r_p = \frac{2\gamma V_L}{RT \ln P/P_o} \cos \Theta + \tau$$

Where r_p is a radius of pore, γ surface tension (8.72×10^{-3} N/m) of the liquid nitrogen, V_L molar volume of the liquid nitrogen, R the gas constant, T absolute temperature, and Θ is the contact angle and assumed to be zero.

τ is the thickness of the adsorbed layer present before capillary condensation takes place. This thickness is calculated by using the Halsey equation [25]:

$$\tau = \sigma \left(\frac{5}{\ln P_o/P} \right)^{1/3}$$

A value of 0.354 nm is used for the average thickness σ of a single molecular layer of nitrogen.

The distribution of pore size can be derived by plotting the increase in pore volume with each smaller pore diameter $\Delta V/\Delta D$ versus the pore diameter. The results obtained on the four samples of natural mineral deposits are summarized in table (3), in which the experimental values of pore volume, pore area, and the most abundant pore radius have been tabulated.

Table (3): The pore volume, pore area and the most abundant pore radius of the different four raw materials deposits.

Parameter	Raw materials deposits			
	Bentonite	Glass sand	Flint Clay	Standard sand
Single point Pore volume	0.4982	0.4521	0.7010	0.5024
BJH Pore volume	0.4101	0.3744	0.6020	0.3900
Pore area	179.72	168.28	140.66	150.67
Most abundant Pore radius	4.1	2.5	6.5	4.9

The results for pore size distribution are also presented in fig (3-a). It had only one maximum for all samples except for samples of glass sand and flint clay which showed two maximum.

The most abundant pore sizes obtained show that most of the pore size are mesopores according to IUPAC definitions.

Mercury Porosimetry

The results of porosity parameters obtained on using the mercury porosimeter to characterize the four deposits have been published in previous work (9-10). The values of pore volume, pore area and the most abundant pore diameter have been tabulated in table (4), while the pore size distributions for these samples are presented in fig (3-b).

Table (4): The porosity parameters of the different types of the raw materials deposits

Sample	Pore volume cc/g	Pore area m^2/g	Most abundant pores nm
Bentonite	0.4169	143.88	12.9
Glass sand	0.3784	151.36	38.0
Flint clay	0.6089	101.48	8.1
Standard Sand	0.3942	121.30	2.2

Comparison

Although, both methods for pore structure analysis are based on surface tension, capillary forces and pressure, the results of the two methods can be compared. The comparable parameters are total pore volume, pore size distribution and specific surface area.

The total specific surface area are measurable by N_2- gas adsorption technique, but this parameter cannot be surface to the area of the geometric shape may be taken as the roughness factor for that surface [26].

The total pore volumes as measured by the two techniques agree within (0.01 cm^3/g); the pore volume measured by mercury porosimetry is slightly higher, possibly because this is an extremely wide-pored deposits, with some pores too wide to be measured by nitrogen sorption. Mercury porosimetry is applied over a pore diameter range from 3nm to 360 µm, while the physical adsorption of N_2 gas technique can extend the lower size measurement down to about 0.35 nm diameter but the upper size is 300 nm.

The curves of the pore size distributions measured by the two techniques (figs3), show that are different although the total pore volumes are similar, and a three distinct regions are observed. The first region is at high pore diameter which shows that the distribution have an extremely a wide range for mercury porosimerty. The second region is associated with the pore diameter range from (3-300 nm), and show that the distribution are similar. On small pore size (the third region) the examination produces a different picture. Pore size distribution measured by mercury intrusion are significantly lower than those measured by nitrogen adsorption. This observation suggests that the samples of natural deposits have a micro and mesopores and that no intrusion has measured by mercury porosimetry technique. However, the high difference between the pore surface area and the total surface area indicate that the deposits used in this work have a small relative porosity. This may be used to define a measure of surface roughness. If the nominal external envelope of the solid has a well defined geometric shape, then the ratio of the area of the external adsorbent taken place when the upper pressure limit of the porosimeter has been reached.

Conclusions:-

The main conclusions that can be drawn from the foregoing results and discussions may be formulated as in the following paragraphs:-

1- The Gas adsorption and mercury porosimetry are complementary techniques. The determination range of mercury porosimetery is wider than that of nitrogen adsorption, and mercury porosimetry determines larger pores that are out of the detection range of nitrogen adsorption. With nitrogen adsorption, the smallest pores that are out of range of mercury porosimetry, can be determined.

2- The pore size distribution are equal on two techniques when pore size ranges from 3 to 300 nm are compared, but the results obtained do not agree on higher or lower this range.

3- With large-pore size, the pore values of such materials measured by mercury intrusion can be greater than those determined from nitrogen adsorption because a significant fraction of pores lies outsides the nitrogen adsorption measurement range. Hence the pore size distributions measured by mercury intrusion can be more useful than the nitrogen adsorption results. When the pore size of the materials is very small, the nitrogen adsorption method is the only appropriate techniques for this type of pore. As such, mercury intrusion is inappropriate for determining pore size distribution of these materials, because the pore size is outside the range analysis.

4- The total specific surface area of the materials measurable by nitrogen adsorption techniques, while the pore surface area of such materials can be measured by the two techniques.

5- The total pore volumes as measured by the two techniques agree within 0.01 cm^3/g.

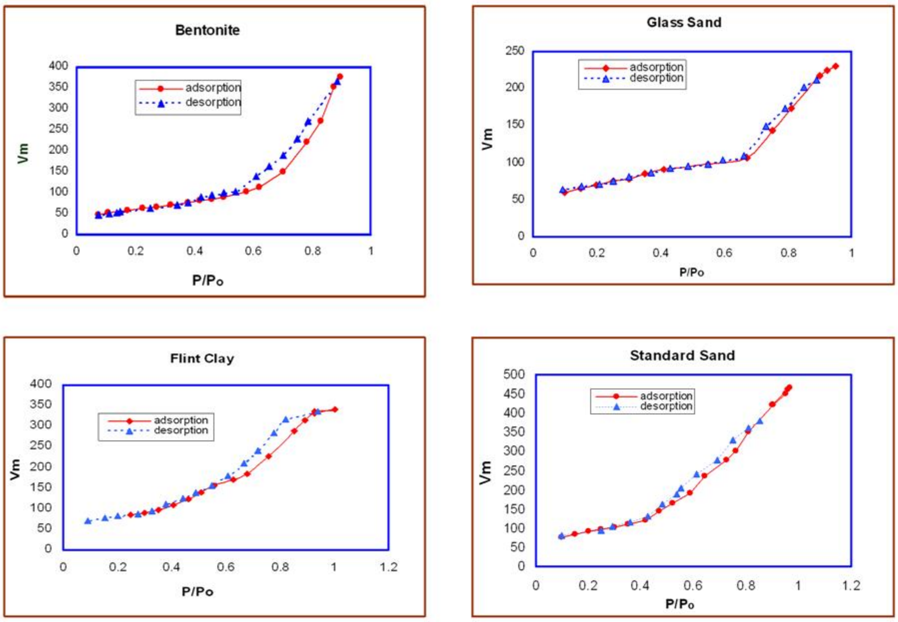


Fig (1): Adsorption - desorption isotherms of Nitrogen gas at 77K of the four types of the deposits.

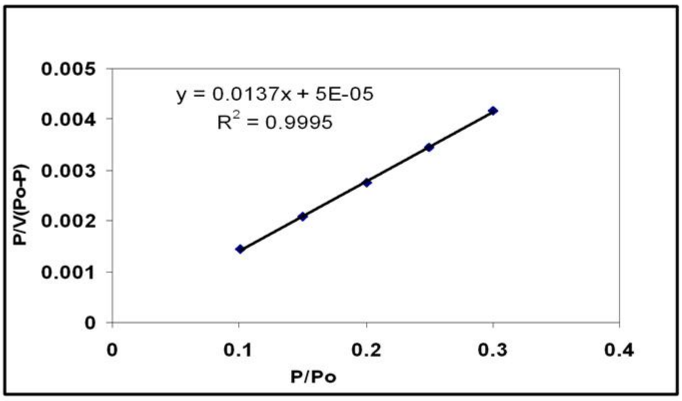


Fig (2): BET surface area plot for Bentonite deposit.

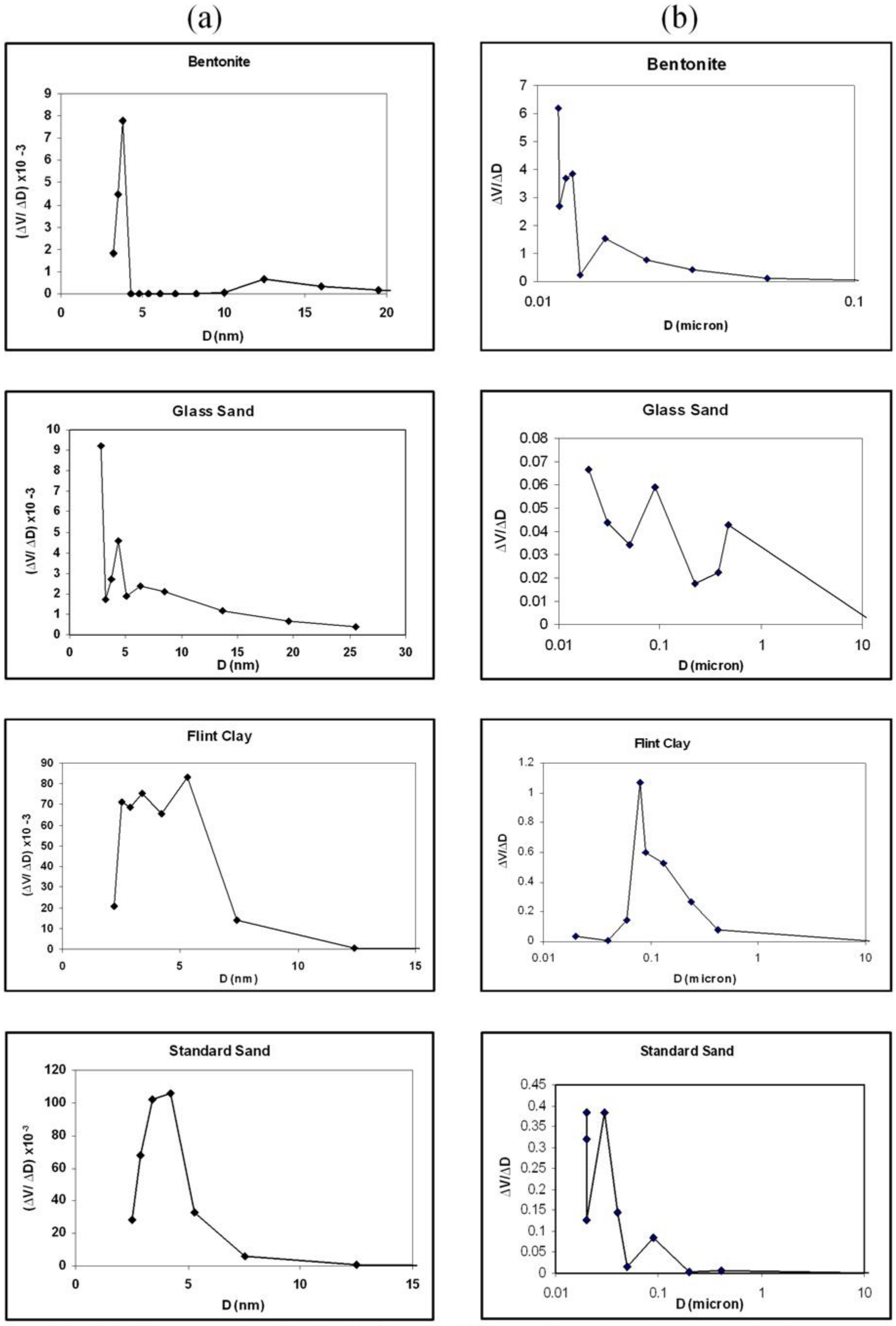
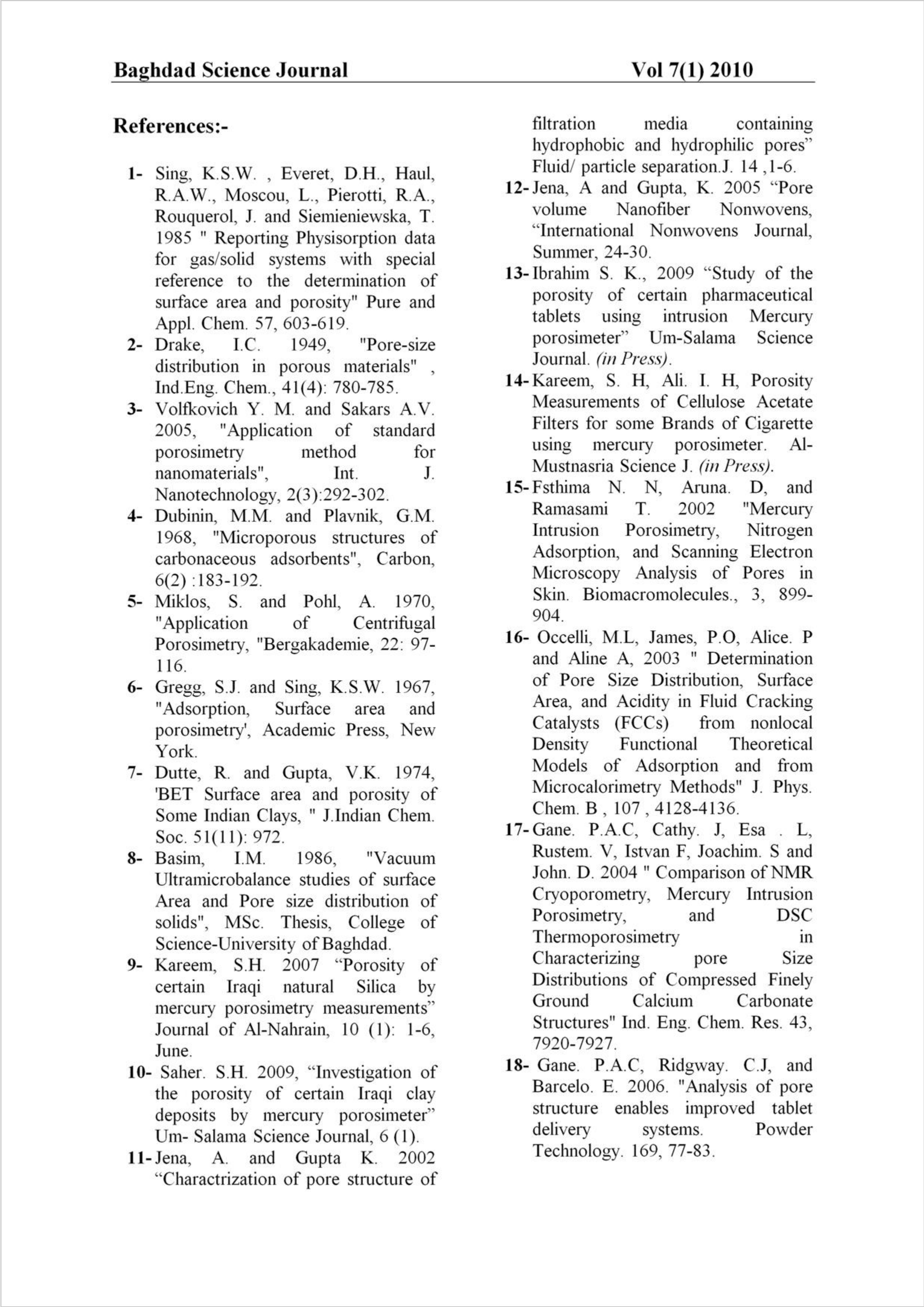


Fig (3): The pore size distributionfor the different four deposits obtained using:
(a) Nitrogen gas adsorption (b) Mercury intrusion porosimeter.



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مقارنة بين قياسات نفاذ الزئبق وأمتزاز النتروجين في تشخيص ترسبات معينة من الخامات الطبيعية

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الخلاصة :

لمسامية المواد اهمية في العديد من التطبيقات والمنتجات والعمليات، مثل معدات الكيمياء الكهربائية كألاقطاب والاغشية والمكونات الفعالة في البطاريات. وتظهر هذه الاهمية كذلك في الاغشية المسامية الرقيقة والسيراميك والتربة ومواد البناء وغيرها. شخصت مسامية هذه المواد بطرائق متعددة اهمها طريقتا امتزاز النتروجين والمقياس الزئبقي للمسامية ذات الاهمية الكبيرة للاغراض الصناعية. في هذا البحث ، استخدمت كلا التقنيتين لتشخيص بعض ترسبات الخامات الطبيعية العراقية، وهي رمل الزجاج و الرمل القياسي و الطين الحراري والبنتونايت.

وقد تم اختبار ومناقشة المعلومات التي حصلنا عليها من كلا التحليلين على الانواع المختلفة من ترسبات الخامات. وأظهرت حسابات المساحة السطحية النوعية اختلافا محسوسا لنتائج كلا الطريقتين على نفس المواد، مما يدل على ان لهذه المواد مساحة سطحية خارجية لم نتمكن من قياسها بطريقة مقياس المسامية الزئبقي. وكذلك اظهرت نتائج توزيع حجوم المسام التي حصلنا عليها بطريقة امتزاز غاز النتروجين مدى واسع من حجوم المسام الاصغر مما يدل على ان لهذه المواد مسام مجهرية حسب تعريف الــ IUPAC لحجوم المسام.