An Adsorption Method for Characterization of Surface Area and Pore Size of Solid Surfaces

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This study focuses on an adsorption method aiming surface characterization of porous solids. Natural Albanian clay, activated carbon and a medicinal Albanian plant are considered for the current characterization. These materials are widely used in chemical industry. The surface characterizations of these porous materials intend the determination of specific surface area, total volume of pores and the distribution of pores by size. The above-mentioned determinations make possible the prediction of these porous materials behavior during physico-chemical processes carried out on their surfaces. Their characterization is carried out using the method of gases adsorption. In this context nitrogen is used as adsorption gas at 77 K. We found size of pores in the order of nanometer scale.

Keywords: Surface characterization, Gases adsorption, Size of pores.

INTRODUCTION

Knowledge of the properties of the pore structure of solid materials is highly important for the development of catalytic materials and catalysts. The assessment of the dynamic changes of these catalytic materials under reaction conditions is extremely important especially for catalysis and for industries generally. Aiming to give a brief guideline on how to use an adsorption method for the characterization of the surface area and pore size of several solid materials we considered for the current application rosemary plant, natural clay and activated carbon. In particular clays and activated carbon are an excellent choice for the study of surface phenomena due to their high porosity. Additionally, plants are also considered as solid porous materials with an increased interest in different fields of industry and they serve as well, as a good probe for the study of surface phenomena[1]. Plants of Albania fauna (for example, *Rosmarinus officinalis*) show characteristics of Mediterranean area. Rosemary (*Rosmarinus officinalis*) is a woody herb with fragrant, green and needle-like leaves and white, pink, purple or blue flowers, native to the Mediterranean region. The leaves are used to flavor various foods, like stuffings and roast meats. Rosemary contains antioxidants such as carnosic acid and rosmarinic acid and other bioactive compounds including camphor, caffeic acid, rosmaridiphenol and rosmanol. Some of these may be useful in preventing or treating cancers, strokes and Alzheimer's disease[2]. Clays have the unique capability of expanding in the presence of water and contracting in its absence. As it is well known, clays are hydrous aluminium silicate and are classified as phyllosilicates. They have a layered structure which can be described as constructed from two modular units: A sheet of cornerlinked tetrahedra and a sheet of edge-linked octahedra. Each tetrahedron consists of M^{x+} cation, coordinated to four oxygen atoms and linked to adjacent tetrahedral by sharing three corners[3]. Activated carbon, also called activated charcoal or coal, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. Activated carbon is obtained by the pyrolysis of natural or synthetic organic polymer materials. Mostly natural material is used which can range from coconut shells to wood. Following the pyrolysis activation consists of controlled oxidation[4] at, *e.g.*, 900 °C.

Surface modifications of porous materials require determination of specific surface area, general volume of pores and the distribution of pores according to their range. Specific surface area and pore size distributions of micropores and mesoporous materials are best probed by nitrogen[4]. Surface area characterization for the solid porous materials in this work is also carried out by nitrogen gas adsorption method and intends the determination of specific surface area, total volume of pores and distribution of pores by size. Adsorption isotherms obtained throughout this work describe relation between the amounts of molecules adsorbed on a unit (mass, surface) of the solid and the sorbate equilibrium pressure (or relative pressure) at a given temperature[4]. The majority of isotherms which result from physical adsorption may be grouped into six classes, *i.e.*, the six types included in the classification originally proposed by Brunauer, Deming, Deming and Teller[5].

The essential features of sorption isotherms are indicated in Fig. 1. Type-I isotherms are obtained when adsorption is limited to, at most, only a few molecular layers[7]. This condition encounters in chemisorptions, where the asymptotic approach indicates that all surface sites are occupied. In the case of the physical adsorption, sorption isotherms obtained on microporous materials are often of Type-I. Type-II isotherms are typically obtained in case of non-porous or macroporous adsorbents where unrestricted monolayer-multilayer adsorption begins to occur. The B point indicates the inflection point. At this point the monolayer coverage is complete and multilayer adsorption begins to occur. Type-III is a rounded shape and does not exhibit a point B. This indicates that attractive adsorbate-adsorbent interactions are relatively weak and adsorbate-adsorbate interactions play an important role. Type-IV isotherms are typical for mesoporous materials. The most characteristic feature of the Type-IV isotherms is the hysteresis loop, which is associated with the occurrence of pore condensation[7]. The initial part of Type-IV can be attributed to monolayer-multilayer adsorption as in the case of the Type-II isotherm. Type-V isotherms show pore condensation and hysteresis. Nevertheless, on the contrary to Type-IV the initial part of this isotherm is related to adsorption isotherm of Type-III, indicating relatively weak attractive interactions between the adsorbent and the adsorbate[7]. Type-VI isotherm is a special case, which represents stepwise multilayer adsorption on a uniform non-porous surface[8], predominantly by spherically symmetrical, non-polar adsorptives.
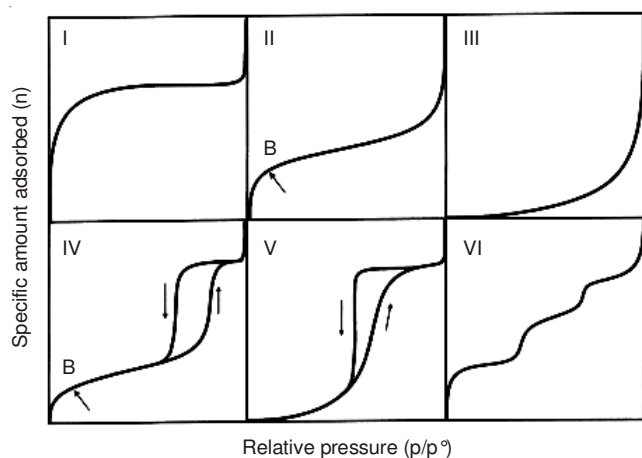

Fig. 1. IUPAC (International Union of Pure and Applied Chemistry) classification of sorption isotherms[6]

The individual pores in heterogeneous catalysts and in other porous technical substances may vary significantly in size and shape. A classification of pores according to their average width was originally proposed by Dubinin[9] and has now been officially adopted by the International Union of Pure and Applied Chemistry[10]. According to this classification, the width of micropores range from 0.3 to 2 nm, mesoporous substances have pore sizes from 2 nm to 50 nm and macropores range from width of 50 nm up to about 105 nm. Additionally, the BET[11] equation is still most generally used method for the determination of specific surface areas. The range of partial pressures where theory and practice are in reasonable agree-ment is limited, *i.e.*, from p/p₀ 0.05 to 0.34. p_0 is referred to saturation pressure, whereas p is referred to the equilibrium pressure. Additionally, the porosity is referred to the empty area of pores in a material. Interior surface of material contain pores and cracking that are deeper than the width. All the parameters determined by nitrogen adsorption method are compared between each other for the three porous materials examined in this study.

EXPERIMENTAL

Rosemary plant (*rosmarinus officinalis*) used in this work is a local Albanian plant. The leaves of the plant are used for surface characterization prior to grinding and drying. The drying process is carried out at room temperature under vacuum. In order to preserve the structure of the leaves, drying at elevated temperature is avoided. Natural clay is also local Albanian clay and used such as prior to drying. Natural material (wood) is used to supply carbon. Activated carbon is prepared as described elsewhere[12]. Natural clay and activated carbon has been dried in thermocouple furnace (150 °C) under vacuum (10^{-5} atm).

Adsorption-desorption isotherms are measured using nitrogen as adsorptive gas (from 0 to 1000 mbar) in boiling temperature of liquid nitrogen. A newly set up has been constructed for this purpose. The set up includes a gas vessel which can be connected to gas supplies up to 1000 mbar pressure and a vacuum system (Fig. 2). The sample under study can be inserted in a sample container which can be connected afterwards to the set up *via* valve 1 (V1) as indicated in the scheme of Fig. 2. During the measurements the sample container remains dipped in liquid N_2 bath (77 K, boiling point). The set up system is initially flushed thrice with N_2 prior to vacuum. The sample container is also vacuumed and after the removal of nitrogen gas in the set up (last flush), the system can be pressurized at the desired pressures to start though the adsorption process. Nitrogen gas is introduced in the set up at values up to –10 mbar pressures. Once the system has reached the equilibrium (p) the system is pressurized yet again to another –10 mbar of pressure. The set up is allowed yet again to reach equilibrium (p). The latter can be checked by the digital sensor pressure (pressure gauge). The pressure is gradually increased likewise up to 300 mbar. Above this value nitrogen was allowed to flow in the system at pressures up to 100 mbar. Adsorption process was finished at 1000 mbar N_2 pressure. Desorption process was carried out similarly merely in the reverse order. The pressure was allowed to drop slowly by vacuuming. As in the case of adsorption, during desorption process the system was allowed to reach equilibrium before decreasing the pressure in the next step. The equilibrium pressure is reached when capillary (pore) condensation phenomenon occurs. Capillary condensation represents a phenomenon whereby gas condenses to a liquid-like phase in pores at a pressure less than the saturation pressure (p_0)[7]. The values of equilibrium pressures obtained during the desorption processes (measurements) are used in the upcoming paragraph for the calculations of the total volume of pores and pores size. Adsorption-desorption isotherms are plotted based on the pressure values obtained from the adsorption-desorption measurements.
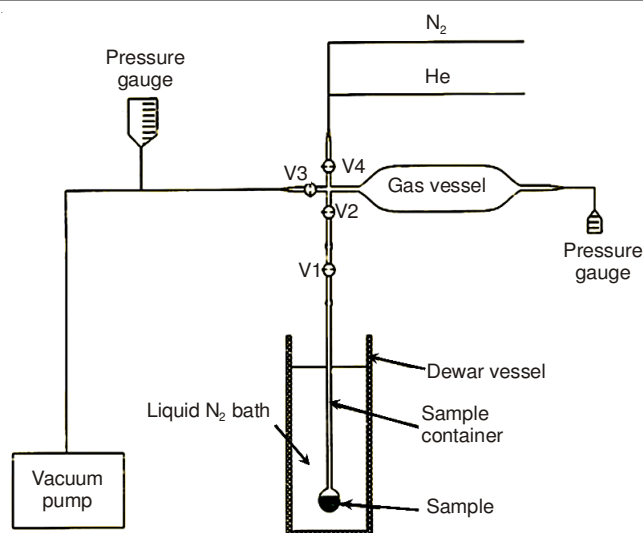
Fig. 2. Set up of N_2 adsorption gas in 77 K

RESULTS AND DISCUSSION

Adsorption-desorption isotherms: Nitrogen adsorption-desorption isotherms as function of relative pressure at -196 °C for rosemary, clay and activated carbon are shown in Fig. 3a-c. According to IUPAC classification which recommends six types[6,10] of sorption isotherms the observed isotherm for rosemary plant belongs to Type-III, without inflection point (Fig. 3a). The sorption isotherm for the natural clay belongs also to Type-III (without inflection point) as it can be seen in Fig. 3b. Lastly, the observed isotherm for the activated carbon (Fig. 3c) is classified as the Type-II with inflection point. The inflection point indicates the stage at which monolayer coverage is complete and multilayer adsorption begins to occur as already noted in the introduction.

Specific surface area determinations: Fig. 4a-c displays BET plots for the determination of specific surface are of rosemary, clay and activated carbon respectively. The graphs in Fig. 4 plot $\dfrac{P}{N(P_0 - P)}$ *versus* P/P_0 where N is number of moles of N_2 adsorbed, P is equilibrium pressure of adsorbates in the temperature of adsorption (obtained from the measurements) and P_0 is saturation pressure of adsorbates in the temperature of adsorption (obtained from the measurements). As known BET theory postulates that under dynamic equilibrium conditions the rate of adsorption in each layer is equal to the rate of desorption from that layer[4]. Molecules in the first layer are located on the sites of constant interaction strength and the molecules in that layer serve as sorption sites for the second layer and so forth. The surface is, therefore, composed of stacks of sorbed molecules. Lateral interactions are assumed to be absent. With these simplifications one arrives at the BET equation[11]:

$$\frac{P}{N\times(P_0 - P)} = \frac{N\times C\times\dfrac{P}{P_0}}{\left(1 - \dfrac{P}{P_0}\right)\times\left[1 + (C-1)\times\dfrac{P}{P_0}\right]}$$

or rearranged into linear form: $\dfrac{P}{N\times(P_0 - P)} = \dfrac{1}{C\times N} + \dfrac{(C-1)\,P}{C\times N\,P_0}$
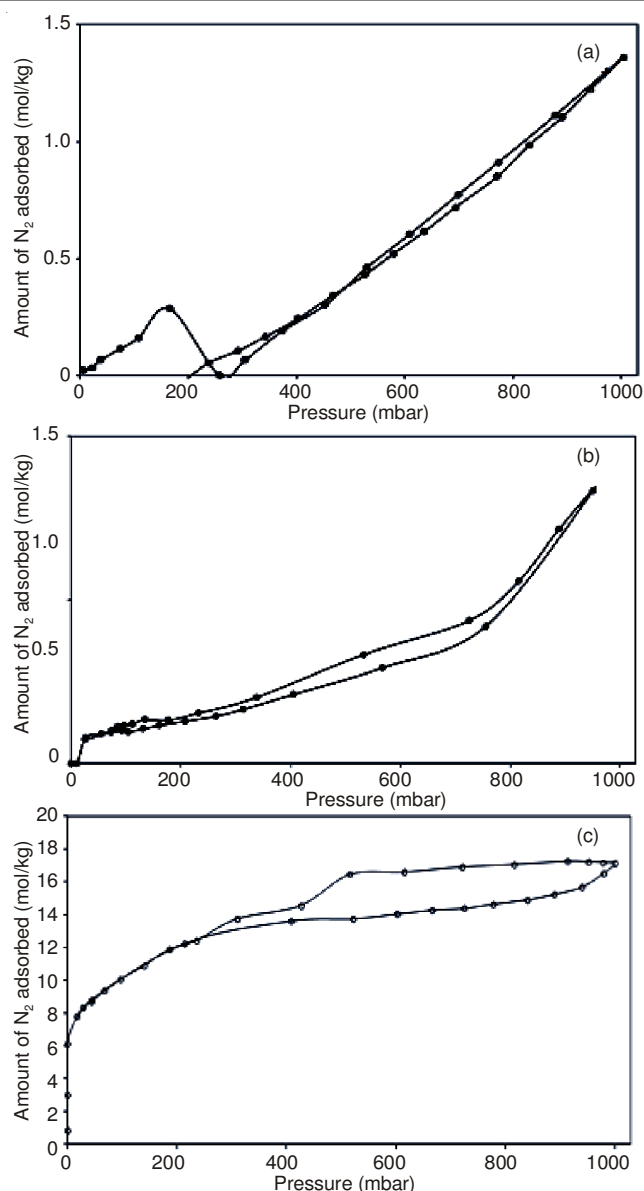

Fig. 3. Nitrogen adsorption-desorption isotherm for (a) rosemary (b) clay and (c) activated carbon. The upper curves belong to desorption isotherms, whereas the lower curves belong to adsorption isotherms

where N is number of moles of N_2 adsorbed, P is equilibrium pressure of adsorbates in the temperature of adsorption, P_0 is saturation pressure of adsorbates in the temperature of adsorption. The quantity C approximates to $C = e^{-\frac{(\Delta H_A - \Delta H_C)}{RT}}$, where ΔH_A is heat of adsorption and ΔH_C is heat of condensation. The difference between ΔH_A and ΔH_C becomes smaller with increasing the pressure, whereas C becomes smaller than 1. The intercepts in the plots of Fig. 4 provide the ratio: $\dfrac{1}{C\times N}$ whereas the slopes (tangent of the angle) provide the ratio: $\dfrac{C-1}{N\times C}$. In this way one can readily calculate N (number of moles of N_2 adsorbed) and C. Finally, specific surface area (BET surface area) for the three samples may be calculated by the following formula[11]: $S_{specific} = N\times N_{Avogadro}\times\omega_0$, where, N is number of moles of N_2 adsorbed (calculated from the

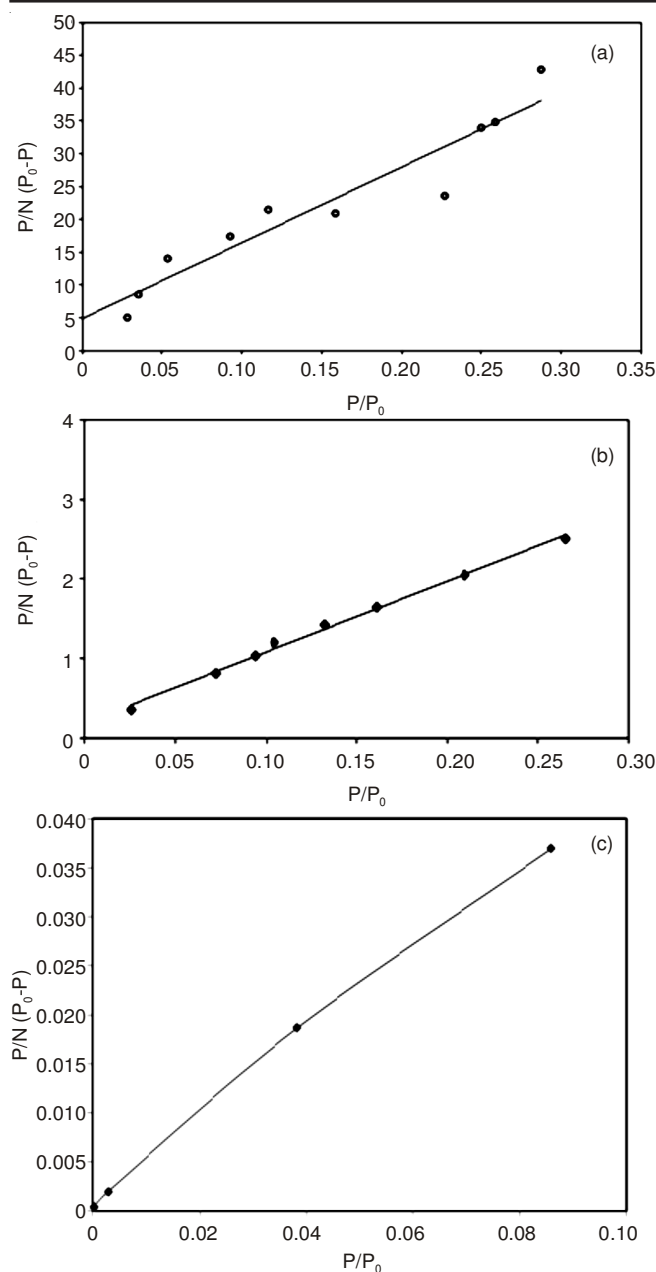Fig. 4. BET plots for (a) rosemary (b) clay and (c) activated carbon

Fig. 5. Differential pose size distributions of (a) rosemary (b) clay and (c) activated carbon

slope of the plots in Fig. 4 as mentioned), $N_{Avogadro} = 6.02 \times 10^{23}$ mol^{-1} and ω_0 is surface of $N_2 = 16 \times 10^{-20}$ m^2. From the BET plots and the above mentioned formulae the following values were obtained for specific surface areas of rosemary, clay and activated carbon: 0.2635, 13 and 1200 m^2/g, respectively. Reported value for bentonite (clay)[3] is in the range of 28 m^2/g which is in reasonable agreement with our finding. Reported values of activated carbon[4] and activated carbon hollow fibers[13] are in the ranges of 500-1200 and 269-1422 m^2/g, respectively, which are in good agreement with our finding (1200 m^2/g). Studies on surfaces area determinations of plants are very limited, however the much lower value of surface area obtained for rosemary in comparison to natural clay and activated carbon is very realistic bearing in mind the porosity of the clay and activated carbon.

Pore size distribution: Fig. 5. show graphs of differential pore size distribution of (a) rosemary, (b) clay and (c) activated
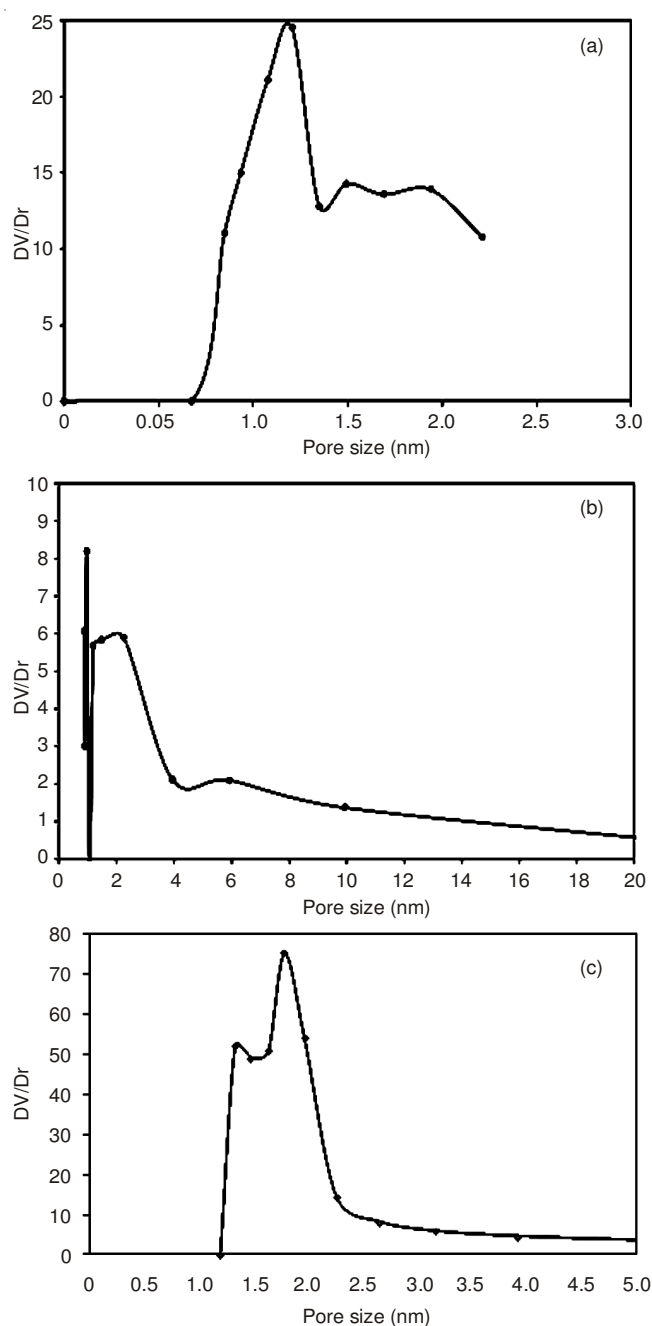
carbon. Pore radii and pore volume distributions as a function of the pore radii (pore size) may be calculated from the relative pressures at which pores are filled and emptied. For the case of pore filling with liquid nitrogen, the relation between the pore radius and relative pressure at which filling starts $\left(\dfrac{p}{p_0} \right)$ is given by the Kelvin equation[4,7]: $r_{capillary} = \dfrac{-2 \times \sigma \times V_{molar}}{R \times T \times \ln\left(\dfrac{p}{p_0} \right)}$ where V_m equal to 34.6 cm^3/mol is the molar volume of condensed liquid nitrogen, R, the gas constant equal to 8.314 J K/mol and T =

77 K boiling temperature of nitrogen and surface tension of liquid nitrogen (σ) is equal to 8.85×10^{-3} N/m. Pore radii is equal to capillary radii plus thickness of adsorption layer $\left(r_{pores} = r_{rapillary} + t_{ads} \right)$. Thickness of adsorption layer may be calculated from the relative pressure $\left(\dfrac{p}{p_0} \right)^{4,7}$.

The differential pore size distribution of rosemary (Fig. 5a) shows that the major part of pores is micropores with capillary size up to 1.2 nm. Nevertheless, the range of size pores varies from 1.2 to 2.2 nm which also belongs to the micropores area. In the case of natural clay two sharp peaks are observed in Fig. 5b, in the ranges of pores size 2.2 nm and < 1 nm. The distribution of the natural clay shows microporous porosity as well. However, pores up to 20 nm are observed as well from the plot in Fig. 5b. The latter is an indication for the presence of mesoporosity in the natural clay. Stankovic *et al*.[3] reported for bentonite clay microporous porosity (2-4 nm) with a certain amount of mesoporosity. Additionally, differential pore size distribution of activated carbon is associated with the presence of two peaks in the region of 1.3 and 2 nm (Fig. 5c). The second peak appears sharper and extends up to 5 nm pore size. This result is indicative of a certain amount of meso-porosity in addition to microporous pores present in the activated carbon. Kaludjerovic *et al*.[13] reported size of mesopores in the range 2-12 nm, which is in reasonable agreement with our finding.

Pore volume distribution: As a final point, pore volume (total volume of pores) distributions are plotted in Fig. 6 for the three samples (rosemary, clay and activated carbon). The total volume of pores may be determined by the equation[7]:

$V_{total} = V_{molar} \times N$, where N is number of nitrogen moles adsorbed calculated by the ratio of $\dfrac{P}{P_0}$. The total volume of pores for rosemary is about 18 cm³/kg (Fig. 6a). In the case of natural clay the total volume of pores reaches a maximum of about 27 cm³/kg. It is indicative from Fig. 6b that integral pore size distribution of clay has the form of Langmuir isotherm. Activated carbon has the largest total volume of pores *i.e.*, 176 cm³/kg and integral pore size distribution has the form of Langmuir isotherm (Fig. 6c).

Conclusion

Various materials were considered to test the newly constructed set up for the determinations of specific surface area, sizes determinations and pore volume distributions. The adsorption of nitrogen at 77 K used in this work represent a typical physical adsorption process and it the most recent method for the porous solid characterization. The overall results indicated in Table-1 clearly prove the viability of the method used. It is concluded from Table-1 that activated carbon appears the most porous material as expected. We found pores in the micro-porous range, however a certain amount of pores in the meso-porous range was evident as well.
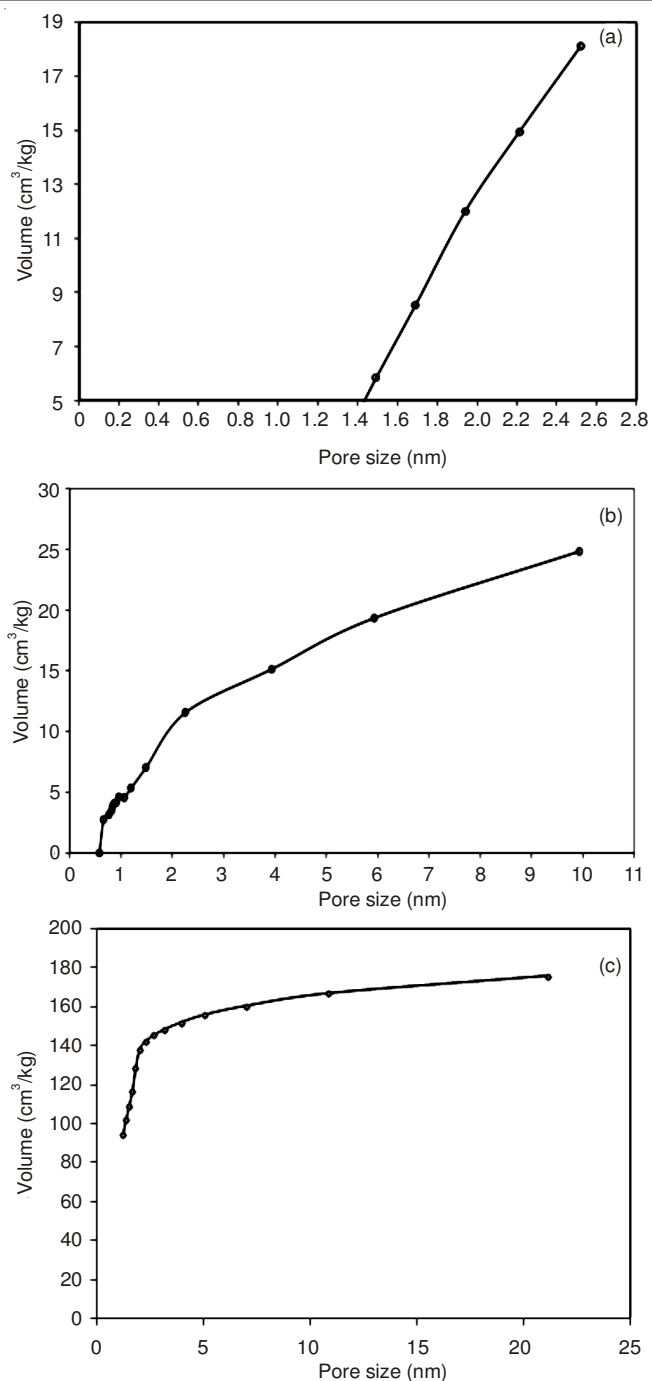

Fig. 6. Integral pore size distributions of (a) rosemary (b) clay and (c) activated carbon

TABLE-1
OVERALL ASSESSMENT OF THE SAMPLES CHARACTERIZED BY NITROGEN ADSORPTION AT 77 K

	Rosemary	Natural clay	Activated carbon
Specific surface area (m²/g)	0.3	13	1200
Maximum value of pore size (nm)	1.2	2.2	2.2
Total volume of pore size (cm³/kg)	18	27	176

Finally, the complete determination of the total pore volume and size determination of mesopores and macropores requires application of mercury porosimetry. Nevertheless, we limited ourselves only to nitrogen adsorption at 77 K methodology.

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