Physical properties of mesoporous scoria and pumice volcanic rocks

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Keywords: volcanic rock, scoria, pumice, BET surface, pore size, mesopore, pore volume

Abstract
In this study, the chemical composition, crystal structure, texture properties, and thermal properties of five powdered samples of scoria and pumice volcanic rock from different Harrats were investigated. It was observed that volcanic rocks show variations in chemical compositions, crystal structure, texture, and thermal properties. All samples comprised SiO₂, Al₂O₃, CaO, and Fe₂O₃ as the major elements and contained both amorphous and crystalline phases. Textural parameters such as surface area and porosity were determined using various calculation models. The surface area of scoria samples was between 0.85 and 1.71 m² g⁻¹ (Brunauer–Emmett–Teller and Single point model), 0.293–1.028 m² g⁻¹ (Barrett–Joyner–Halenda model), and 1.02–2.35 m² g⁻¹ (Langmuir model). While for pumice, the calculated values of the surface area were 1.67 m² g⁻¹ (Brunauer–Emmett–Teller and Single point model), 0.763 m² g⁻¹ (Barrett–Joyner–Halenda model), and 2.24 m² g⁻¹ (Langmuir model). The adsorption–desorption isotherm curves reveal that the scoria and pumice particles under study have mesoporous sizes between 7.89 and 9.81 nm, respectively. The differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) results of scoria and pumice samples illustrate a thermally stable material at high temperatures. TGA results show a weight gain by about 1.0% has been observed in the scoria samples in the region beyond 600 °C that may indicate a probable oxidation phenomenon with a change in color. While the DSC results of the red scoria and pumice did not show any recrystallization or oxidation, but only showed a small loss of weight in the TGA result. The diversity in molecular composition, texture, and structure of scoria and pumice volcanic rock samples provide for promising natural stable mesoporous materials that can be used in various mesoporous technologies or applications such as solar cells.

Nomenclature

| Symbol | Description |
|--------|-------------|
| Q      | the adsorbed volume at equilibrium of adsorption (cm³ g⁻¹) |
| Qm     | the adsorbed volume of a monolayer (cm³ g⁻¹) |
| K      | equilibrium constant of adsorption |
| P      | equilibrium pressure (MPa) |
| P₀     | saturated vapour pressure (MPa) |
| P/P₀   | the relative pressure |
| S      | specific surface area (m² g⁻¹) |
| Nₐ     | Avogadro’s number |
| a      | the sectional area of a nitrogen molecule (0.162 Å²). |
| mₛ     | mass of the adsorbent sample (g). |
| Vₘ     | the molar volume. (22.414 cm³ mol⁻¹). |
| C      | the BET constant |

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1. Introduction

Volcanic rock is a material primarily composed of aluminum silicate in a crystalline or amorphous form. It has been studied and used in some applications for several years ago [1, 2]. Volcanic rocks can be used for several industrial purposes including cleaner substances and polishing compounds, they may be used as an ingredient in asphalt, and in agriculture as fertilizer. Additionally, they may also be used for painting, construction, insulation, and fillings purposes, solar cell, and volcanic gas reservoirs [3–8]. The required application of volcanic rock depends on geometric shape (particle size and surface area) in addition to chemical and mineral composition [9, 10]. Most volcanic rocks contain a wide spectrum of silica, alumina, iron oxides and other oxides in minor proportions. The mineralogical composition and properties of the volcanic rock depend on the origin of the magma and eruption conditions [11].

Volcanic rocks commonly come in the form of scoria and pumice [12, 13]. The scoria has colors ranging from black to poorly red while the pumice has colors from black to white with a porous or vesicular structure [14, 15]. Pumice is a volcanic rock that is abundantly present and therefore inexpensive, consisting of various chemical compositions that vary depending on its location. Because of its global availability, pumice has been used in many fields such as environmental and industrial applications [16–18].

Volcanic rock often contains a high content of silica. Scoria and pumice both contain high amounts of silica ranging between 40–52 wt% and 63–75 wt%, respectively [19, 20]. Silica production from inexpensive substances has received great interest due to its economic value comparing to other methods such as sol-gel process that produce silica from tetraethyl-orthosilicate [21, 22], or from quartz-sand in alkali and high-temperature environment [23]. However, the current traditional and commercial methods are still expensive and energy consuming, hence the volcanic rock of both types may be an appropriate and inexpensive source of silica.

The volcanic rocks of scoria and pumice have a porous structure which makes them easier to develop and therefore more attractive to various applications [15]. Porous materials, in general, are classified according to the size of their pores into microporous in which their pores are in the range of 50 nm, mesoporous which are the materials with pores ranging between 2–50 nm, and finally microbores which are materials with pores less than 2 nm. Besides, the term of nanomaterials includes all substances with pores up to 100 nm [24]. Mesoporous materials are characterized by distinct pore sizes and unique designs, which allow them to interact with atoms and molecules in a manner that leads to separation or hosting of the molecules to be isolated for specific applications. To make the most from porous materials, it must have two properties, a sufficient number of pores in addition to the fact that pores must provide an improved adjustment to the performance of the material. The channels and cavities of the mesoporous materials have the ability to selectively separate ions and molecules according to their different sizes, which can be used in many applications such as energy efficiency and catalysis [25].

The specific surface area plays a key role in determining the efficacy of the rock in several applications, where increasing the surface area of particles will increase their ability to adsorb, making the material susceptible to applications such as water purification. It has been emphasized that the use of fly ash will solve waste disposal problems and act as inexpensive materials to adsorb water pollutants [26]. Adsorption is a surface phenomenon which depends on the surface area, the distribution of particle size, and the porosity of the adsorbent material. In some studies, it has been observed that the specific surface area is directly proportional to the contents of carbon and inversely to the size of the adsorbed particles [27]. The specific surface area and chemical properties of fly ash have been extensively studied in many studies. In contrast, volcanic rock has not undergone sufficient studies related to particle morphology and chemical properties. This study aims to extensively evaluate the textural,
chemical, and thermal properties of five types of volcanic rock collected from different regions. The chemical analysis of the volcanic rocks was performed using x-ray fluorescence spectrometry (XRF), and the crystal structure was achieved using x-ray diffraction (XRD). Thermal Analysis was carried out using Differential scanning calorimetry (DSC). Surface area, pore-volume, and pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) method. Furthermore, the relationships between pore diameters, specific surface areas, and pore volumes were investigated. Also, the relationships between chemical composition and thermal properties were discussed investigated.

2. Experiment

2.1. Materials
Five samples of volcanic rock were collected from different Harrat that locates in Saudi Arabia. Harrats are rich with pyroclastic volcanic rock materials. The five sample of volcanic rocks were cleaned and dried, and then grounded to fine powder (particles size = 3.5–7 μm (using crusher unit and a smoothing machine Pulverizers agate (ROCKLABS, New Zealand) to prepare for the measurement [2]. The raw and powder of five samples of volcanic rock are shown in figure 1. The location, color, density and type of volcanic rock are shown in table 1.

2.2. Characterization techniques
The chemical compositions of the samples were determined by x-Ray Fluorescence (SPECTRO—EXPOS) in order to determine the major and minor elements (expressed as % oxides). The crystalline phases and mineralogical were studied using XRD with a Bruker D8 Advance XRD (Bruker, USA), Cu Kα Ni-filtered radiation with a wavelength of 1.54 Å. The thermal properties were investigated in static air. The thermal measurement of 0.300 mg sample placed in an alumina crucible was carried out with a heating rate of 5 °C min⁻¹ at the temperature rang starting from room temperature up to 1300 °C using TGA-DSC NETZSCH model STA 449 F3 Jupiter (NETZSCH- Germany). Thermal analysis was used in order to study how the samples
change with temperature. In particular, thermogravimetric analysis (TGA) was used to probe the changes of the mass sample as a function of the temperature in order to determine the thermal stability of the samples. While DSC was used to measure the changes in the heat flow to and from a sample as a function of the temperature. DSC provides useful information about samples such as solid-liquid phase transition (melting points, freezing, or crystallization), solid-solid transition (cold crystallization, or changes between different polymorphs), glass transition. Textural properties such as specific surface area, pore volume, pore size and particle size of the samples were determined from the N2 adsorption–desorption isotherms at 77 K by Micrometerics ASAP 2020 equipment. About 0.6 g of sample was placed in glass tub (inside diameter = 9.53 mm) to be degassed and analyzed using Micrometerics ASAP 2020 equipment. Before measurements, the samples were automatically degassed under vacuum for about six hours in to remove water and other contaminants from the surface of samples in order to get accurate measurement. The cold and warm free space was 46.7856 cm$^3$ and 15.7232 cm$^3$, respectively. The dead volume of the sample was calibrated before and after each measurement using helium gas that is used for a blank run, because helium does not adsorb onto the sample. In the nitrogen adsorption method, the partial pressure gradually increases at a constant temperature, and the adsorbed amount is measured at each corresponding time point. Then, the data collected is displayed as an isothermal adsorption curve that plots the amount of gas adsorbed as a function of the relative pressure. This experiment was carried out with ultra-pure nitrogen (N$_2$ > 99.999%) which is usually used due of its availability in high purity and its strong interaction with most solids for measurable amounts of adsorption to occur.

### 3. Results and discussion

#### 3.1. Chemical properties and crystal structure

The chemical composition of the volcanic rock samples determined using XRF for major and minor elements (expressed as wt% oxides). Although XRF does not indicate the mineral phases distinctly, it gives the information related the existing of different minerals in the oxide forms, which help determine the possible mineral phases in correlation with diffraction data. Table 2 showed that (powder) volcanic rock contains SiO$_2$, Al$_2$O$_3$, CaO, and Fe$_2$O$_3$ as major elements; and K$_2$O, MgO, MnO, Na$_2$O, P$_2$O$_5$, TiO$_2$, and SO$_3$ as minor elements. Based on this data and content of the silica, it is clear that the sample S2 is pumice, and the other samples are scoria. It can be distinguished between pumice and scoria based on the content of the silica. If the content of silica in the volcanic rock is larger than 50%, the volcanic rock will be pumice, and if it is lower than 50% will be scoria [19, 20]. The sample S2 has the highest percentage of SiO$_2$, as displayed clearly in table 2, and so the lowest percentage of CaO, MgO, and Fe$_2$O$_3$. The variance observed on the physical appearance of the rocks (such as color) is because of the different chemical composition and mineralogical composition of the volcanic rock which may in turn due to the historical conditions of volcanic eruption and volatile matter from the lower layers of Earth [11]. In general, the pumice contains a high percentage of silica, about 71%, and at the same time it contains high percentages of aluminum, potassium, and calcium, while the percentages of magnesium, and iron are low. For this reason, this type contains high percentages of light-colored minerals. While, the scoria contains less than 48% of silica and is rich in dark-colored minerals due to the high levels of calcium, magnesium, and iron. For example, if a volcanic rock contains a high amount of magnetite (Fe$_3$O$_4$) the color tend to be black, and if a volcanic rock contains hematite (Fe$_2$O$_3$) the color tend to be red. While if a volcanic rock contains a high amount of silica the color will be white. The density values of the scoria samples analyzed in this study were similar, varying between 3.02 and 3.30 g cm$^{-3}$, while the pumice sample showed a lower density (2.73 g cm$^{-3}$). This can be due to the difference in the iron oxide amounts in each sample (table 1), as scoria contains higher amounts of iron oxides than in pumice, varying from 11.47 to 14.66 wt% in scoria and 3.14 wt% in the pumice sample.

Table 2. Major and minor elements in the volcanic rock samples by XRF (wt. %).

| Sample | SiO$_2$ | Al$_2$O$_3$ | CaO | Fe$_2$O$_3$ | K$_2$O | MgO | MnO | Na$_2$O | P$_2$O$_5$ | TiO$_2$ | SO$_3$ | LOI |
|-------|--------|------------|-----|-------------|-------|-----|-----|---------|---------|--------|-------|-----|
| S1    | 44.89  | 15.25      | 8.63| 14.16       | 0.71  | 6.33| 0.19| 4.26    | 0.55    | 3.09   | <0.05| 0.85|
| S2    | 71.62  | 10.87      | 0.42| 3.14        | 3.62  | 0.24| 0.07| 6.08    | 0.22    | 0.15   | <0.05| 2.60|
| S3    | 47.02  | 15.93      | 8.97| 11.47       | 0.94  | 8.30| 0.16| 3.68    | 0.37    | 2.00   | <0.05| 0.18|
| S4    | 46.84  | 16.44      | 7.13| 14.41       | 1.18  | 4.80| 0.20| 4.65    | 0.68    | 2.99   | 0.08 | <0.05|
| S5    | 47.76  | 16.34      | 6.34| 14.66       | 0.52  | 3.57| 0.23| 4.69    | 0.97    | 2.49   | 0.12 | 0.63|

Figure 2 shows XRD patterns of volcanic rocks under study. It can be observed from the figure that there is a presence of both amorphous and crystalline phases in all rocks. However, the samples S1 and S2 have clearly high crystalline phases while S3, S4, and S5 have high amounts of amorphous contents. The major crystalline phases in S1 are albite (NaAlSi$_3$O$_8$), pargasite (NaCa$_2$Mg$_4$Al$_5$Si$_8$O$_{22}$(OH)$_2$), ilmenite (FeTiO$_3$), and hematite (Fe$_3$O$_4$).
(Fe₂O₃). The high content of crystalline ferrous mineral can be understood by noting the content of iron oxides in XRF data in table 2. However, this not the case in samples S3, S4, and S5 where there are high levels of iron oxides (about 11 to 14 wt%) that cannot be observed as a crystalline component in XRD patterns, which indicates their presence in their amorphous form. The specimen S2 is a pumice volcanic that contains an excessive amount of silica, which appears in the form of quartz (SiO₂). Besides, it contains the crystalline minerals albite and anorthoclase (Na,K)(Si₃Al)O₈. The samples S3, S4, and S5 apparently include small quantities of the following minerals: albite and anorthite (CaAl₂Si₂O₈). The diversity in molecular composition and structure of volcanic rock samples gives a variety of possible applications. For example, samples that contain a high content of silica and alumina in their amorphous form such as S3, S4, and S5 can be used in the manufacture of geopolymer by exposing them to an alkaline or acidic environment. However, inorganic polymers cannot be formed using the same minerals when they are in their crystalline forms [26].

3.2. Textural properties

The study of the textural properties of volcanic rock samples involves measuring the adsorption of gases such as nitrogen on the surfaces of the samples. The partial pressure of the gas gradually increases due to its adsorption. The experimental adsorption–desorption isotherms of nitrogen on the five volcanic rock samples are presented in figure 3. The interpretation of the adsorption–desorption isotherms reveals detailed information about main textural parameters, such as specific surface area, specific pore volume, porosity, pore size distribution, and average pore size. The mathematical models, such as the Langmuir model (LA), Brunauer–Emmett–Teller (BET) model, and Barrett–Joyner–Halenda (BJH) model, can be used to calculate the textural parameters from the experimental isotherms. The interaction between a volcanic rock pore surface and nitrogen gas produces a van der Waals force that results in the adsorption of the nonpolar nitrogen gas molecule. This type of adsorption is referred to as physical adsorption [28].

Figure 4 illustrates the characteristic three stages of the isothermal adsorption curves of the volcanic rock sample. At the first stage (Stage 1), before point B on the adsorption curve, the adsorption of the first layer of the nitrogen molecules onto the solid surface occurs. At the second stage (Stage 2), there is multilayer adsorption of the nitrogen molecules, wherein the number of adsorbed layers gradually increases with the increasing relative pressure as does the adsorption capacity. Finally, the third stage (Stage 3) is the nearly vertical ascent stage, wherein the adsorption pressure reaches the saturated vapor pressure of the gas and the nitrogen molecules begin to liquefy and the capacity reaches its maximum adsorption value. Then, the pressure is reduced, and the nitrogen gradually begins to desorb. The adsorption quantity of nitrogen at Stage 1 is generally <0.5 cm³ g⁻¹, <1 cm³ g⁻¹ at Stage 2, while at Stage 3, the maximum adsorption quantities are in the range of 3.4602–5.0277 cm³ g⁻¹ (see figure 3). Various mathematical models such as Langmuir model (LA), Brunauer–Emmett–Teller (BET) model, single-point model, t-plot, and Barrett–Joyner–Halenda (BJH) model used in this study to determine the textural parameters are briefly discussed below. The textural properties of all the volcanic rock samples are presented in table 3.
3.2.1. The Langmuir model

The Langmuir model (LA) is based on the monolayer assumption, that is, the assumption that on a homogeneous surface, there is adsorption of a monolayer of molecules and that all the sorption sites are

Figure 3. Nitrogen adsorption and desorption of volcanic rock samples.
independent and identical. This model is ideal for the study of both chemical and physical adsorption on some microporous materials with pore diameters $<2\text{ nm}$ [29]. The Langmuir isotherm equation is as follows:

\[ \frac{Q}{Q_m} = \frac{K_P}{(1 + K_P)} \]  

Equation (1) can be linearized to obtain equation (2):

\[ \frac{(P/P_0)}{Q} = \frac{1}{QK_P0} + \frac{(P/P_0)}{Qm} \]  

Figure 5 represented the equation (2) with the nitrogen adsorbed volume ($Q$) and the relative pressure ($P/P_0$). The adsorbed volume of a monolayer $Q_m$ can be obtained from the slope of the Langmuir plot. The specific surface area $S$ is determined using the equation (3):

\[ S = \frac{(N_A \times a \times Q_m \times 10^{-20})}{m_s V_M} = 4.35 \text{ Qm} \]  

where $N_A$ is Avogadro’s constant, $a$ is the sectional area of a nitrogen molecule, $m_s$ is the mass of the adsorbent sample, and $V_M$ is the molar volume. The surface area of scoria volcanic rock samples was obtained in the range of $1.02–2.35 \text{ m}^2 \text{ g}^{-1}$, while for the pumice volcanic rock sample, it was $2.24 \text{ m}^2 \text{ g}^{-1}$ (table 3).

3.2.2. The Brunauer–Emmett–Teller (BET) model

The BET model [30] is considered an extension of the LA model from the monolayer molecular adsorption to the multilayer adsorption. The form of the linear equation of the BET is:

\[ \frac{P/P_0}{Q(1 - P/P_0)} = \frac{1}{Qm C} + \frac{(P/P_0)(C - 1)}{Qm C} \]  

where $C$ is the BET constant. Figure 6 shows the BET plot that obtained from a straight-line $P/Q (P_0 – P)$ as a function of $P/P_0$:

\[ Q_m = 1(A + B) \text{ and } C = 1 + \frac{B}{A} \]  

where $A$ is the ordinate at the origin and $B$ is the gradient of the straight line. The BET surface area was determined using equation (3). The specific surface areas of the scoria volcanic rock samples were in the range of $0.85–1.71 \text{ m}^2 \text{ g}^{-1}$, while for pumice volcanic rock sample, it was observed to be $1.67 \text{ m}^2 \text{ g}^{-1}$. These values of the BET surface area were lower than those of the LA surface areas (see table 3). The surface area of Sample S5 ($1.71 \text{ m}^2 \text{ g}^{-1}$) was found to be the largest of all samples. All adsorption average pore widths ($d_{av}$) were calculated using equation (6):

\[ d_{av} = \frac{4V_P}{S_{BET}} \]
Table 3. The textural properties of volcanic rock samples.

| Textural parameters                        | Sample no# | Method                                      | S1    | S2    | S3    | S4    | S5    |
|--------------------------------------------|------------|---------------------------------------------|-------|-------|-------|-------|-------|
| Surface Area(S)                            |            | Langmuir Surface Area (m² g⁻¹)               | 1.6900| 2.2360| 1.2686| 1.0213| 2.3468|
|                                           |            | BET Surface Area (m² g⁻¹)                    | 1.1107| 1.6698| 0.9537| 0.8487| 1.7107|
|                                           |            | Single point surface area (m² g⁻¹)           | 1.1017| 1.6489| 0.9394| 0.8302| 1.6923|
|                                           |            | t-Plot External Surface Area (m² g⁻¹)        | 1.2270| 1.0618| 0.6062| 0.2558| 1.1909|
|                                           |            | BJH Adsorption cumulative surface area of pores diameter (m² g⁻¹) | 0.907 | 0.763 | 0.477 | 0.293 | 1.028 |
|                                           |            | BJH Desorption cumulative surface area of diameter (m² g⁻¹) | 0.6705| 0.7376| 0.5232| 0.3525| 1.4697|
| Pore Volume (Vp)                           |            | Single point adsorption total pore volume of pores less than 77.9710 nm diameter at p/p° = 0.974 531 650 (cm³ g⁻¹) | 0.002 69 | 0.003 34 | 0.002 36 | 0.001 68 | 0.0042 |
|                                           |            | t-Plot micropore volume (cm³ g⁻¹)            | 0.000 04 | 0.000 26 | 0.005 01 | 0.000 24 | 0.000 22 |
|                                           |            | BJH Adsorption cumulative volume of pores (cm³ g⁻¹) | 0.006 61 | 0.006 16 | 0.005 18 | 0.005 48 | 0.007 54 |
|                                           |            | BJH Desorption cumulative volume of pores (cm³ g⁻¹) | 0.006 52 | 0.006 25 | 0.005 25 | 0.005 68 | 0.007 76 |
| Pore Size(dav)                             |            | Adsorption average pore width (4 V S⁻¹ by BET) | 9.7008 | 7.9877 | 9.8780 | 7.8934 | 9.8124 |
|                                           |            | BJH Adsorption average pore diameter (4 V S⁻¹)(nm) | 29.1658 | 32.3176 | 43.4707 | 74.7660 | 29.3214 |
|                                           |            | BJH Desorption average pore diameter (4 V S⁻¹)(nm) | 38.9125 | 33.9113 | 40.1433 | 64.4939 | 21.1164 |
| Nanoparticle Size                          |            | Average Particle Size(nm)                    | 5402.1853 | 3593.1652 | 6291.0377 | 7069.6033 | 3507.2607 |
where $V_p$ is the pore volume. All the samples presented a mesoporous structure (7.89–9.81 nm) according to the conventions of International Union of Pure and Applied Chemistry (IUPAC), thus indicating its low overall density [31–34].
3.2.3. The single-point model

The single-point model considers only a single point \( B \), which is the intersection of the initial concave curve and the linear segment of the S-shaped isotherm. Figure 3 shows that the single point surface area \( B \) of scoria.
samples at \( P/P_0 = 0.1599 \) was in the range of 1.10–1.69 m\(^2\) g\(^{-1}\), and for the pumice sample, it was 1.64 m\(^2\) g\(^{-1}\), which is very close to that of the BET surface area (table 3). The total pore volume of the pores with a diameter less than 77.9710 nm at \( P/P_0 = 0.974 \) 531 650 was in the range of 0.0017–0.0041 cm\(^3\) g\(^{-1}\).

3.2.4. The t-plot model
The t-plot model and its extensions provide a simple means to document the existence of porosity from nitrogen adsorption data. In this model, nitrogen adsorbed volume (Q) at different \( P/P_0 \) values as a function of the layer thickness (t) is plotted. The slope of the t-plot, \( (Q/t) \), is equal to the external surface area, that is, the area of pores that are not micropores (mesopore, macropore, and the exterior surface of the particle) but can form multilayers. This model allows the separation of micropores from mesopores, macropores, and the outside surface using equation (7):

\[
Q\left( \frac{P}{P_0} \right) = Q(\text{micro}) + k S_{ex} \left( \frac{P}{P_0} \right)
\]

(7)

The layer thickness t from equation (7) is substitute with t from the equation of Harkins and Jura [35]:

\[
t = \left[ \frac{13.99}{0.034 - \log \left( \frac{P}{P_0} \right)} \right]^{\frac{1}{7}}
\]

(8)

To estimate the pore size, we use the equation of Halsey [36]:

\[
t = 3.54 \left[ -\frac{5}{\log(P/P_0)} \right]^{\frac{1}{3}}
\]

(9)

This model is valid only within a narrow range of relative pressures (0.20 < \( P/P_0 < 0.50 \)). The slope of the linear t-plot gives the external surface area of the samples (\( S_{ex} \) m\(^2\) g\(^{-1}\)), while the surface of micropores can be obtained from the ordinate at the origin. The external surface area and micropore area of the scoria samples were in the range of 0.2558–1.2270 m\(^2\) g\(^{-1}\) and 0.3475–0.5199 m\(^2\) g\(^{-1}\), respectively. For the pumice sample, the external surface area and micropore area were observed as 1.0618 m\(^2\) g\(^{-1}\) and 0.6080 m\(^2\) g\(^{-1}\), respectively. The sum of the external surface area and micropore area is equal to the BET surface area (\( S_{\text{BET}} \) m\(^2\) g\(^{-1}\)). The micropore volumes of the volcanic rock samples were found to be in the range of 0.000 04–0.005 01 cm\(^3\) g\(^{-1}\) (table 3).

3.2.5. The Barrett–Joyner–Halenda (BJH) model
The BJH model is a statistical method used for calculating the surface area, diameters, and volumes of microscopic pores based on the gas pressure [37]. The effective characterization range of the BJH model ranges from 2 to 100 nm [3]. The cumulative BJH surface area was determined from the surface distribution according to equation (10):

\[
S_{\text{cum}} = \sum \frac{V_{pi}}{r_{pi}}
\]

(10)

The radius (\( r_{pi} \)) is obtained by the Kelvin equation:

\[
r_p = t + r_K = \frac{t - 4.5}{\log(P/P_0)}
\]

(11)

The cylindrical pore radius (\( r_p \)) is linked to the thickness of the adsorbed layer (t), which is calculated using the Halsey equation (9). The pore volume repartition as a function of \( r_p \) is obtained by the derivative of the function (dQ/dr\(_p\)).

The cumulative adsorption surface and pore volume of the scoria samples were in the range of 0.293–1.028 m\(^2\) g\(^{-1}\) and 0.0052–0.0057 cm\(^3\) g\(^{-1}\), respectively (table 3). The cumulative adsorption surface and pore volume of the pumice sample were 0.763 m\(^2\) g\(^{-1}\) and 0.0062 cm\(^3\) g\(^{-1}\), respectively. It was observed that the BJH surface area was lower than the BET surface area (\( S_{\text{cum}} < S_{\text{BET}} \)). The average pore diameters of the samples were calculated using equation (12):

\[
d_{av} = \frac{4V_p}{S}
\]

(12)

From all these models and table 3 provided in this section the following conclusions can be drawn:
i. The adsorption-desorption isotherm curves reveal that the scoria and pumice particles under study have pore sizes between 7.89 and 9.81 nm. Thus, they could be classified as mesoporous materials according to the conventions of IUPAC.

ii. The obtained surface areas for the volcanic rock sample adsorbents were investigated using BET analysis and were found to be in the range of 0.85–1.71 m² g⁻¹, whereas the particle sizes varied between 3500 and 7070 nm, which was the particle size decreased as surface area increased. The particle size and surface area attributes of volcanic rock play a significant role in adsorption applications. The adsorption capacity of the smaller particles is high as they are more reactive; in addition, trace elements tend to concentrate in the finer particles.

iii. Moreover, it was calculated the surface area of scoria and pumice samples using Langmuir model that use for only a single layer (1.02–2.35 m² g⁻¹), Single point model (0.84 and 1.71 m² g⁻¹), and statistical model Barrett–Joyner–Halenda (0.293–1.028 m² g⁻¹). It was observed the calculated surface area of Single point close to BET surface area, while the calculated surface area statistical model Barrett–Joyner–Halenda was lower.

iv. The average pore diameter of the volcanic samples was measured in the range of 29.321–74.766 nm, that is, as the particle size increased, the pore diameter also increased.

v. The specific surface area of volcanic rocks is related to pore volume which increases as the surface area increase. The cumulative pore volume, however, varies between 0.0017 and 0.0042 cm³ g⁻¹.

vi. It appears that the textural properties of volcanic rock are independent of the bulk chemistry. Rather, the small differences observed are likely related to the variations in the crystal-chemical composition of the surface of the volcanic rock.

These conclusions provide a theoretical basis for the exploration of promising natural silica mesoporous applications that use mesoporous technology such as solar cells.

3.3. Thermal properties

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves for volcanic rocks are shown in figures 7 and 8. The TGA curves of scoria samples illustrate a stable to slow loss in mass until it reached about 600 °C, which indicates a highly thermally stable material. However, a weight gain by about 1.0% has been observed in the samples S3, S4 and S5 in the region beyond 600 °C that may indicate a probable oxidation phenomenon and might include the allotropic transformation of iron oxides, this may be confirmed by the observed change in sample’s colors after the thermal test which consistent with recent study [38]. The Samples S1; however, showed a slight degradation and mass loss in the same range of temperature.

DSC results (figure 8) also confirm the previous results where there are exothermic peaks between 700 and 900 °C for the samples S3, S4, and S5 that attributed to oxidation and recrystallization phenomenon during sintering. Generally, an obvious similarity can be noticed in the heat capacity curves of all scoria samples, as there

Figure 7. TGA curves of volcanic rock samples.
is a clear glass transition step in temperatures about 1120 °C, which is attributed to the change of molecular mobility within the material structure. There are also endothermic melting peaks at high temperatures ranging between 1085 to 1260 °C in the volcanic scoria samples, the slight difference in melting points is mainly due to the different chemical composition of each sample. A simple distinction may be indicated in S5, it has a relatively high melting temperature as compared to other samples because of the amorphous nature and amount of silica included.

As for the pumice sample (S2), there is a small mass loss of about 2.8% can be seen in the TGA graph which can be attributed to the removal of OH types related to metal oxides and volatile organic impurities existent in small proportions. This result is consistent with the LOI values of XRF analysis as shown in table 2. The pumice specimen is thermally stable as well with a clear melting point at 1080 °C. A previous thermal analysis study reported that pumice volcanic rock becomes soft at about 900 °C and melts completely at about 1200 °C, that means the pumice can keep its thermal stability until 900 °C [27].

4. Conclusions

The chemical composition, crystal structure, textural and thermal properties of scoria and pumice volcanic rock were investigated. All samples contained both amorphous and crystalline phases and mainly comprised SiO₂, Al₂O₃, CaO, and Fe₂O₃ along with other minor components. The highest quantities in the scoria and pumice samples were those of silica, ranging from 44.89–47.76 wt% and 71.62 wt%, respectively. The quantitative textural characteristics such as surface area and the porosity of the scoria and pumice samples were investigated using different models. The surface area of the scoria and pumice samples was found to be in the range of 0.85–1.71 m² g⁻¹ (BET and single-point models), 0.293–1.028 m² g⁻¹ (BJH model), and 1.02–2.35 m² g⁻¹ (LA model). The adsorption-desorption isotherm curves reveal that the examined scoria and pumice samples have mesoporous structures, according to the IUPAC convention. The average pore diameters, specific surface areas, and specific pore volumes of the volcanic rock samples were found to be correlated. The DSC/TGA results of the scoria and pumice samples illustrate a thermally stable material at high temperatures with some variation between samples. The difference in the thermal properties of the samples was found to be correlated with the chemical composition. The diversity in the molecular composition, texture, structure and thermal properties of volcanic rock samples can open up a wider avenue for various applications. In particular, the low cost, thermal stability, high content of silica, and type of porosity of pumice and scoria make them an excellent natural materials source of high-quality mesosilica that promising for energy and thermal storage applications and in mesoporous technological applications such as solar cells.

Acknowledgments

The authors would like to acknowledge the technical support received from Saudi Geological Survey, the Center of Nanotechnology at King Fahd University of Petroleum & Minerals, and the Center of Nanotechnology at King Abdul Aziz University.
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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