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The Effect of Temperature on the Surface Area and Porosity of TiO_2 Nanoparticle Prepared by sol-gel Method

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Abstract:
TiO_2 nanoparticle has been integrated through synthetic reaction by sol-geltechnique. Thenanoparticles were characterized utilizing techniques like, Scanning Electron Microscope (SEM), atomic force microscope (AFM).UV-visible spectroscopy, X-ray diffraction (XRD), SEM image shows that the TiO_2 is spherical in shape with average diameter different as indicated by temperature, the band gap of TiO_2 nanoparticale is (2.9) eV, BET and BJH investigation gives particular surfacearea. Surface area and Pore volume diminishes with expanding temperature

Keyword: *TiO_2 nanoparticle, Sol-gel, Surface area, Temperature*

1. Introduction

Nanotechnology, this theoretical ability was considered as right on time as 1959 by the renowned physicist Richard Feynman.
Semiconductor nanoparticles have opportunities much enthusiasm amid the previous decade because of their unrivaled size dependent chemical and physical properties (1)
In the most recent couple of years, major efforts have been made to change over the band structure of TiO_2 to shift its absorption edge across the visible light region and place its band edges at proper positions, thus beneficent its photocatalytic efficiency one way of doing so is to dope TiO_2 with either anions or cations. (2)
TiO_2 has three crystalline various anatase, rutile and brookite of these forms, anatase TiO_2 has been most excessively used as a popular catalyst because of its various merits, such as visual and electronic properties, high photocatalytic activity, low cost, nontoxicity and chemical stability. Titanium dioxide is one of the most opportunities materials in nanoscience and nanotechnology because of having a lot of interesting properties from fundamental.
The catalytic activity of TiO_2 is contingent on its specific surface area, which is certainly dependent on the crystal size the smaller the catalyst, the larger will be its surface area. (3)
Many methods have been established for titania synthesis such as sol-gel technique hydrothermal method, chemical vapor deposition, direct oxidation and others.
The sol-gel technique is one of the most used methods due to its possibility of deriving unique metastable structure at low reaction temperatures and excellent chemical homogeneity. (4)
The sol-gel process is the most successful for preparing nanosized metal oxide semiconductor, forexample, sol-gel derived TiO_2 powders have been reported to show high catalytic activity due to their fine structure, wide surface and high porosity. (5,6)
The sol-gel process is a low temperature route most excessively used to obtain better ceramic. (7)

2. Experimental

2.1. Chemicals and Materials

All reagents consumed were of analytical grade purity and were procured from Merck chemical Reagent Co.LTD. titanium tetra isopropoxide(TTIP) (Sigma,Aldrich), ethanol absolute (Merck) and distilled water used for the preparation of nanoparticles by the sol-gel.

2.2. Characterization

The prepared crystalline nanoparticles structure was characterized using Surface morphology was studied by using SEM(Sigma). UV-visible absorption spectrum of nanocrystal is recorded in the wave length range (200-800nm) (100 Conc/Varian. USA) and the average particle size were measured using atomic force microscope (AFM) AA300 scanning probe microscope angstrom Advanced Inc. The surface area of nanoparticles was studied by using Instrument NOVA station A by nitrogen gas

The synthesis of TiO_2 was obtained from titanium tetra isopropoxide (TTIP) was dissolved in absolute ethanol and deionization water was added to solution in terms of a molar ratio of Ti: H2O = 1:4 Nitric acids was used to adjust the pH and for restrain the hydrolysis process of the solution. The solution was vigorously stirred for 60 min in order to form sols. After for 24 hours the sols were transformed into gels. In order to obtain nanoparticles, the gels were dried under 80^0C for 2 hours to evaporate water and organic material to the maximum extent. Then the dry gel was calcination at different temperatures for 2 hours were subsequently carried out to obtain desired TiO_2nanoparticles. (7,8)

3. Results and Dissection

Figure (1) shows the XRD patterns with calcination at (400,500, 600, 700, and 800^oC) for two hours.

From XRD spectrum of TiO_2 sample calcined at 400^oC and 500^oC, the anatase phase was only observed. The main diffraction peaks at 2 θ = 25.46, 38.01, 47.15 and 54.67 ^{o} corresponding to (101), (004), (200) and (105) planes respectively. While titanate phase could transform to anatase phase at the calcination temperature 600^oC (92.59%). The diffraction peaks at 2 θ = 25.2, 37.9, 47.96 and 55.4 ^{o} corresponding to (101) , (004) , (200) and (211) planes to anatase phase , as the diffraction peaks at 2 θ = 27.3 and 54.2 ^{o} corresponding to(110) and (211)planes for rutile phase ,the calcination temperature at 700^oC (84.75%) formed rutile phase and (15.25%) anatase phase The diffraction peaks at 2 θ = 27.48, 36.14, 41.2 and 56.7 ^{o} corresponding to (110) ,(101), (111) and (220) while the diffraction peak at 2= 55.2 ^{o} corresponding to corresponding to (211)for anatase phase ,When the calcinations temperature reached 800^oC only rutile phase was found in the XRD pattern . The main diffraction peaks at 2 θ = 27.6 ,36.2, 41.3, 44.2, 54.4, and 56.8 ^{o} corresponding to (110), (101), (111), (210), (211) and (220) planes.

The effect of phase in good agreement with the results of Abbad et al (9) that all the samples heated to 500^oC show only anatase phase. The samples annealed at 800^oC having higher particle size than those 600^oC, calcination is a common treatment that can be used to improve the crystallinity of TiO_2 particles (10). The crystallite size can be determined from the classical Scherrer formula.

/ B cos **θ**. …... (1)ℷ K D= is the wave length of the X- rayℷ Where D is the crystallite size,

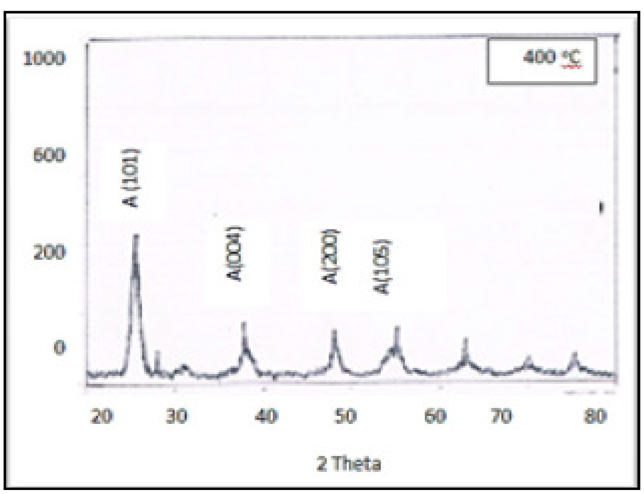
radiation (CuK α = 0.15418 nm), K is the Scherrer constant and B is the full width at half –maximum height, θ is the Bragg diffraction angle. The contents of anatase and rutile of all TiO_2 samples was calculated as following equation (2).

$X_A = 100/ (1+ 1.265\ I_R/I_A)$ ……. (2)

Where X_A is the weight fraction of anatase in the mixture, IA and IR are the intensity of anatase and rutile (11). Table (1) the properties of TiO_2nanoparticles by using equation (2)

Calcinations Temp.(^oC)	Crystalline size (nm)	Anatase %	Rutile %
400	4.93	100	-
500	15.412	100	-
600	21.46	92.59	7.41
700	23.375	15.25	84.75
800	38.077	-	100

Table 1: Summary of the properties of TiO_2 nanoparticle and particle size from XRD diffraction



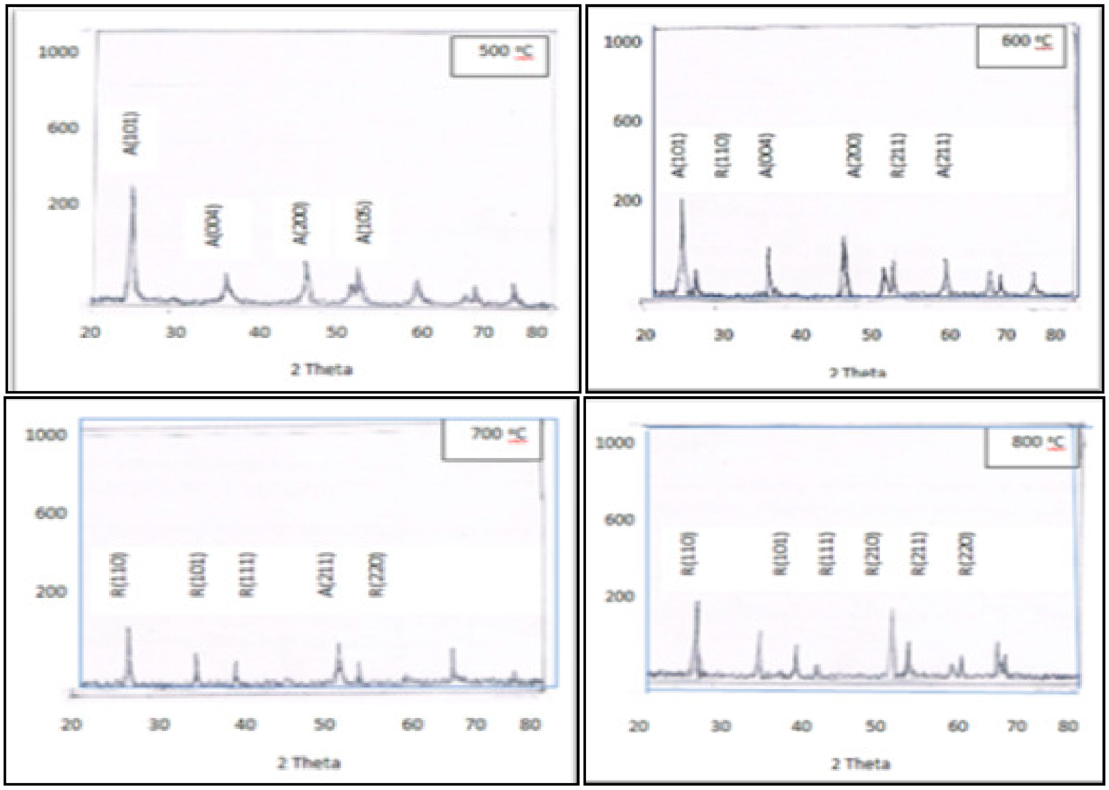
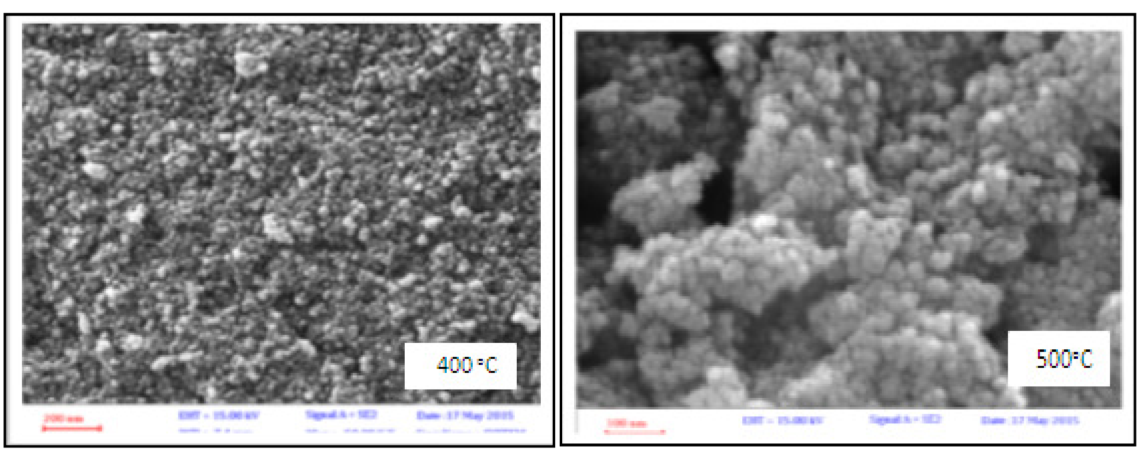


Figure 1: X-ray diffraction (XRD) of TiO_2 nanoparticles at different temperatures

Fig (2) shows morphology of the TiO_2 nanoparticle at different calcination temperatures. When the calcinations temperature was increased to 500^{o}C the surface morphology of the calcined sample consisted of TiO_2 particles with a wide particle size. Increasing the temperature to 600 ^{o}C, the smaller This can be attributed to the phase transformation of
anatase to rutile phase, from 600^{o}C to 800^{o}C the surface morphology of the calcined sample had been changed tobigger particlesize. The structure was difficult to be seen and became smaller than that at 500^{o}C. This is result in agreement with the result of study synthesis of nanostructure TiO_2 film prepared by sol-gel Spin coating method (4) The effects of heat treatment on particle size of TiO_2 nanoparticles as shown in table (2)

Calcination Temp.(^{o}C)	Particle size (nm)
400	28.5
500	50
600	40
700	67
800	75

Table 2: the particle size of TiO_2 nanoparticles at different calcination temperatures



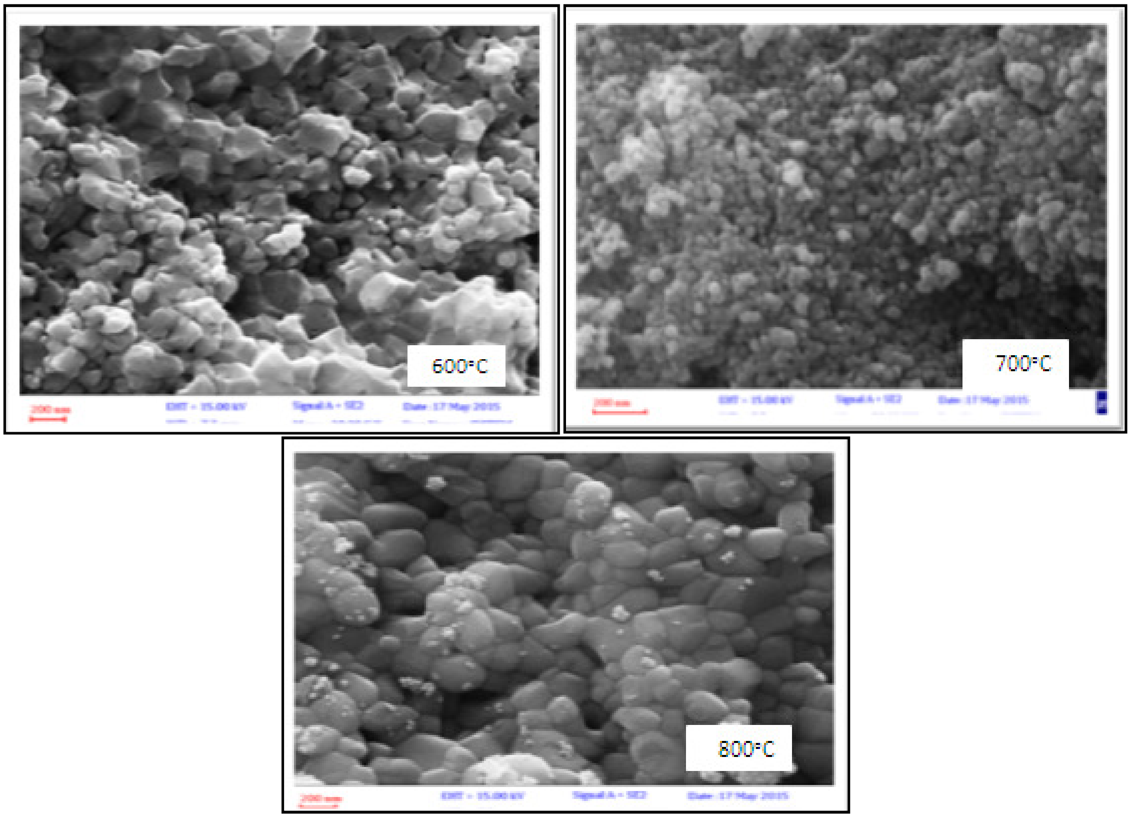
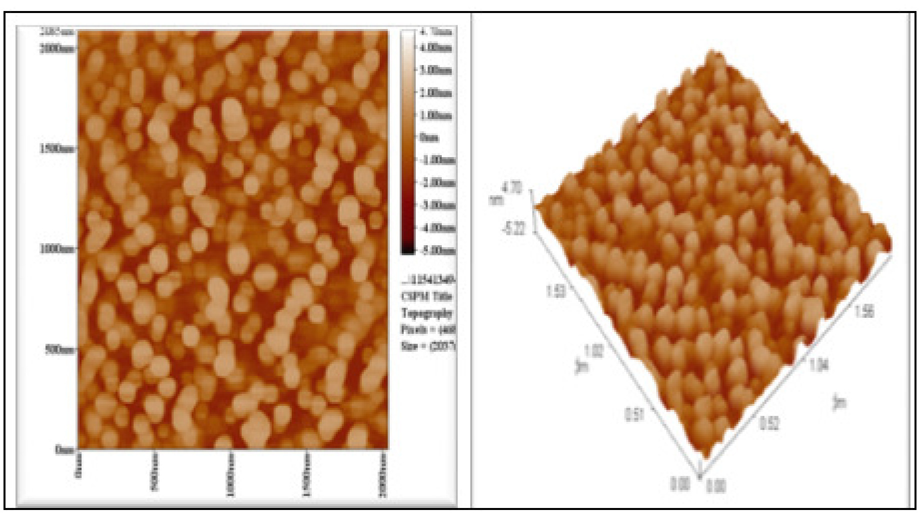
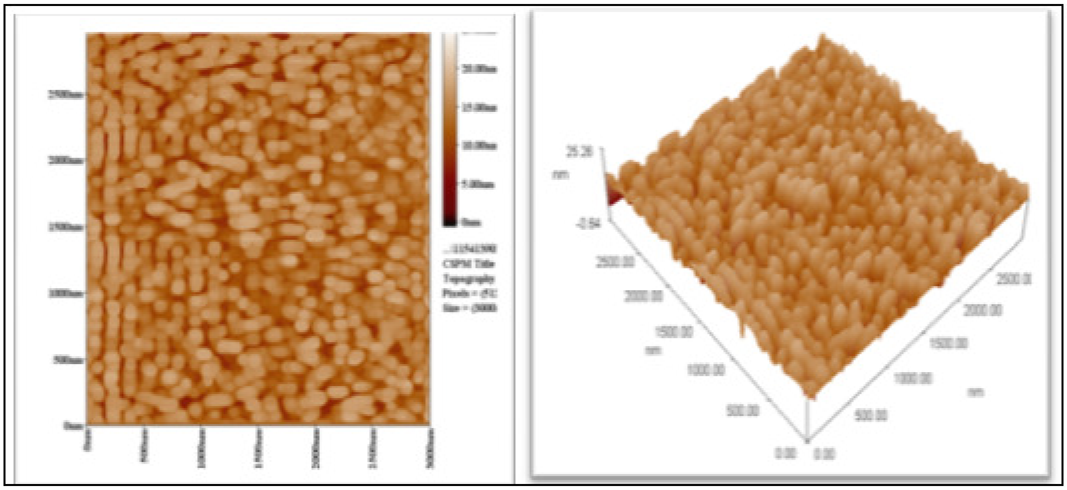


Figure 2: SEM images of TiO_2 nanoparticles calcined at 400· 500· 600·700^oC and 800^oC.

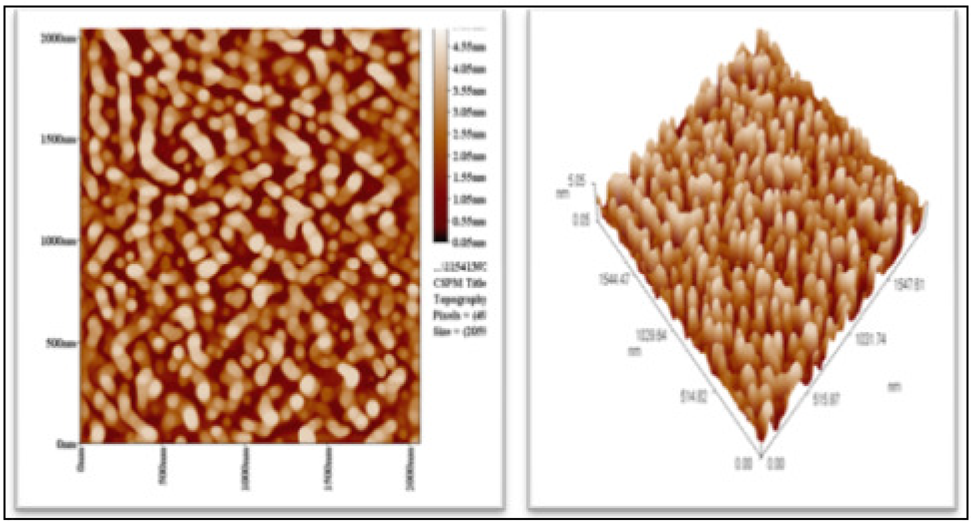
Figure(3) shows the AFM images for different temperature at 400,500,600,700,and 800^oC and corresponding size distributions of the TiO_2 nanoparticles, from figure that TiO_2 nanoparticles are spherical in shape having diameter of (90.36, 94.76, 73.62 ,82,and 86.77nm) according to temperature(400,500,600,700,and 800^oC) that these observed average dimeter increased from 400^oC to 600^oC then decreased at 600^oC and then from 600^oC to 800^oC increased due to transformation of phase from anatase phase to rutile phase.



A



B



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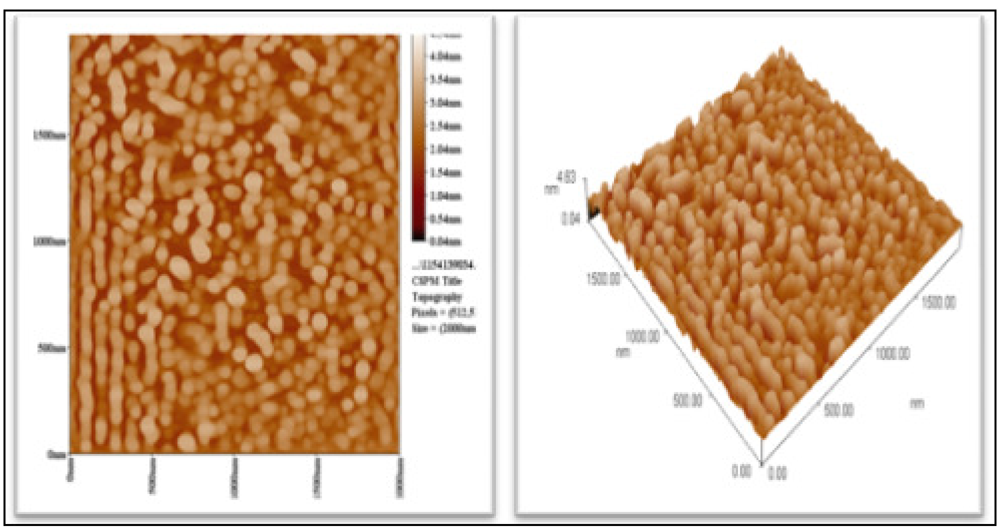

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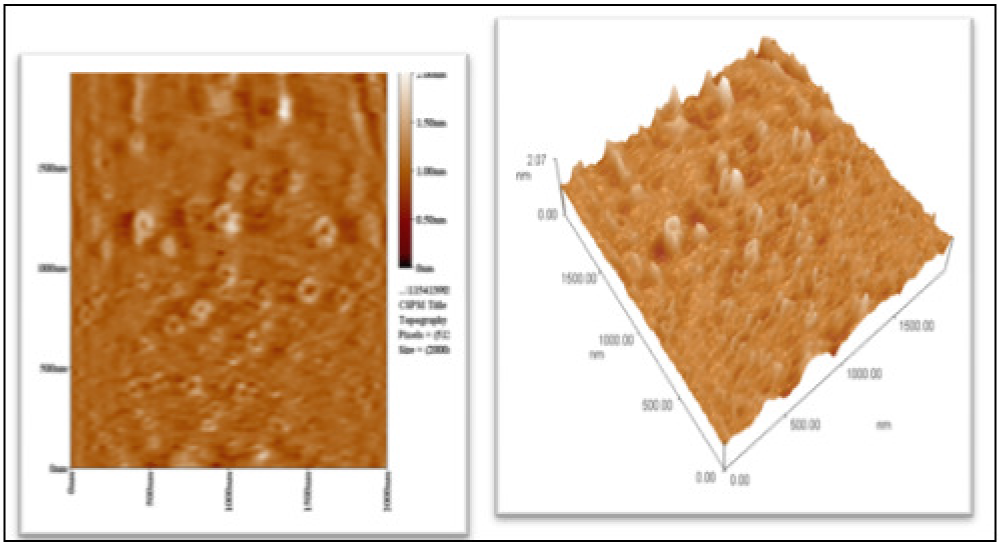


E

Figure 3: AFM image of a prepared TiO_2 nanoparticles (A)400^oC ,(B)500^oC,(C) 600^oC,(D)700^oC and(E)800^oC.

The UV-Visible absorption spectrum leads to the presence of nano crystallines. The energy band gap was measured using the absorption spectra of the nanoparticles. The band gap of the synthesized nanoparticles is calculated using Tausc relation (12).is described as

$(\alpha hv)^{1/n}$ =A(hv-Eg) ……… (3)

Where α is absorption coefficient, A is constant and Eg is the band gap of the materials and exponent (n) that depends on the kind of transition .to locate the possible transition $(\alpha hv)^2$ vs hv is plotted and congruent band gap were obtained from the graph on hv axis the band gap value of TiO_2 nanoparticale is form to be (2.9) eV this value is shifted compared with pure TiO_2.

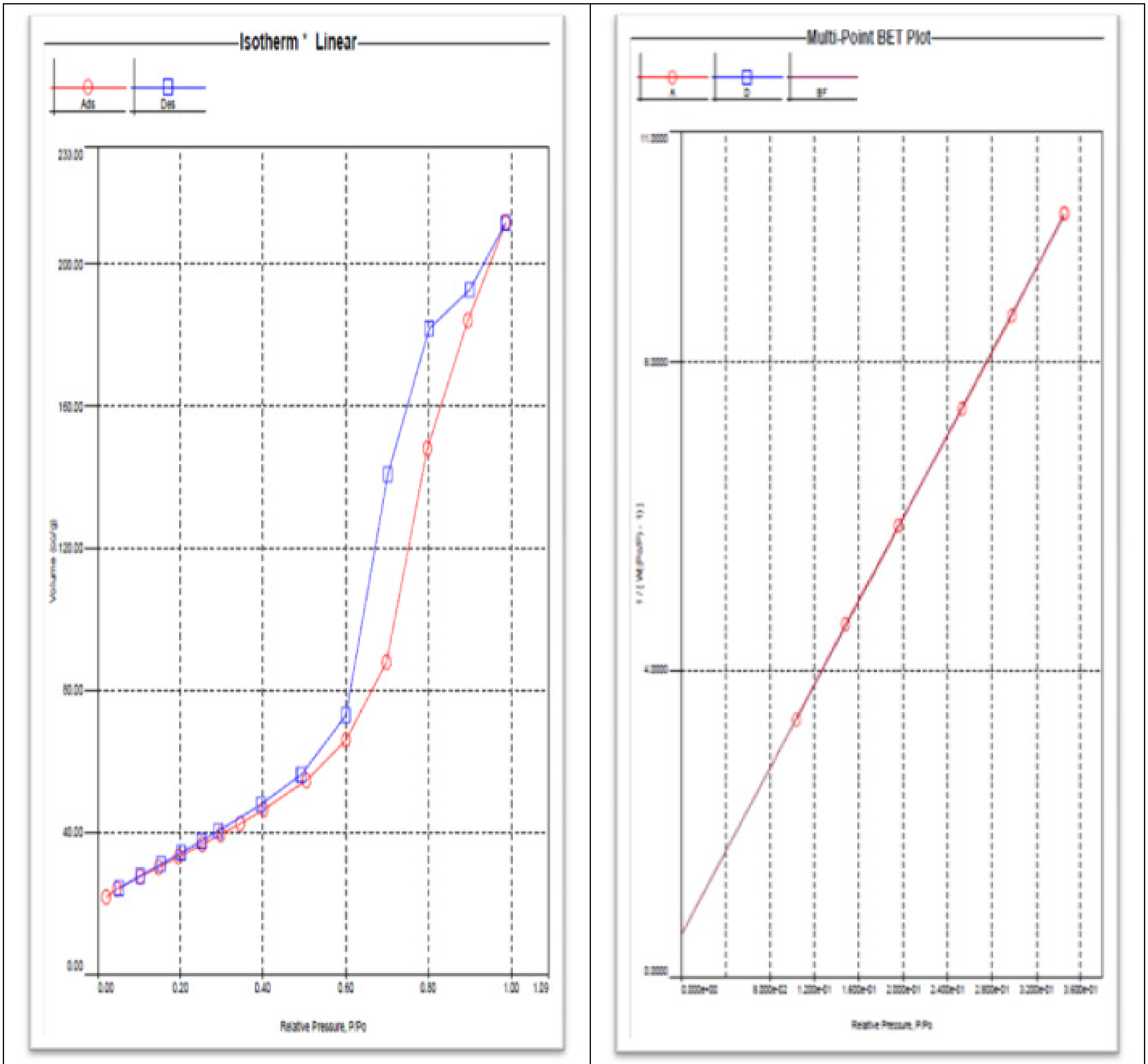
BET and BJH analysis provides specific surface area evaluation of materials and also be employed to determine specific pore volume using adsorption and desorption techniques by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer, the effects of temperatures on surface area and pore volume of TiO_2 nanoparticles were illustrated in table (3)

Temp. (^{o}C)	**Specific surface area (m^2. g^{-1}) BET**	**Specific surface area (m^2. g^{-1}) BJH**	**Total pore volume (cm^3.g^{-1})**	**Pore volume (cm^3.g^{-1})**
400	129.8	190.384	0.3284	0.3528
500	61.60	92.047	0.1639	0.1683
600	24.48	26.90	0.0999	0.1013
700	2.339	3.306	0.03179	0.0320
800	1.418	2.339	0.00478	0.0054

Table 3: The effects of temperatures on surface area and pore volume of TiO_2 nanoparticles

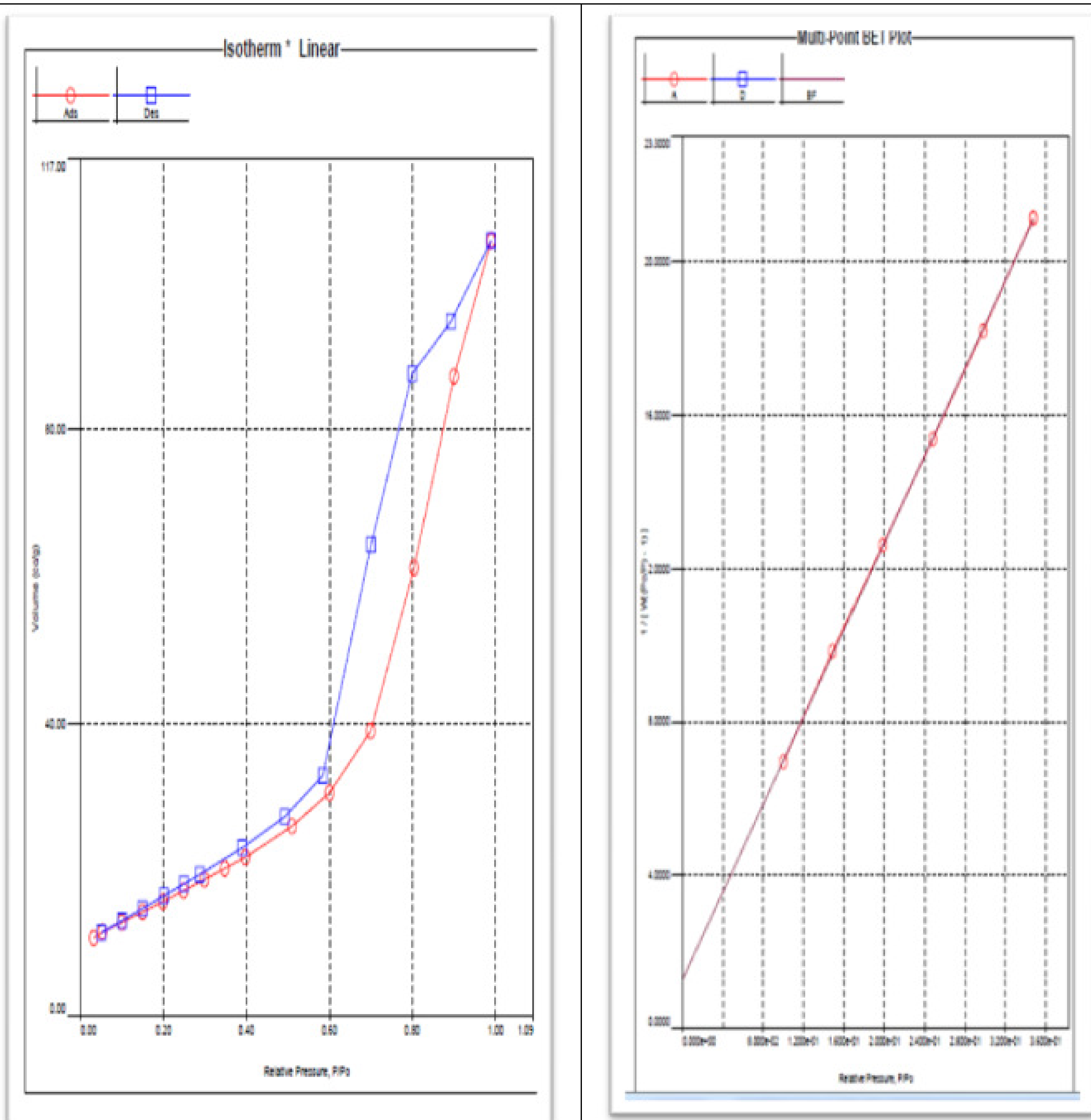
This results indicated that surfacearea and pore volume decreased with increasing calcination temperature. The prepared photocatalysts as mesoporous materials using technology synthesis. The adsorption hysteresis curve type showed that the photo catalyst had cylindrical pore geometry of uniform size.

Sun et al (13),also studied the effect of calcination temperature on photocatalytic activity of Sn(IV)/ TiO_2/AC on the photocatalystis degradation of orange G .their results showed that photocatalytic activity was influenced by the calcination temperature the optimal calcination temperature was 550^{o}C , Akpan and Hameed(14) studied the influence of calcination temperature on the photocatalytic degradation of organic pollutants using TiO_2 .In their investigations the effects of calcinations temperature on the surface area ,pore volume the results observed the surface area and pore volume decreased with increased calcinations temperature at 400^{o}C to 850^{o}C .Figure (4) showing the isotherms of different TiO_2 samples calcined at different temperature



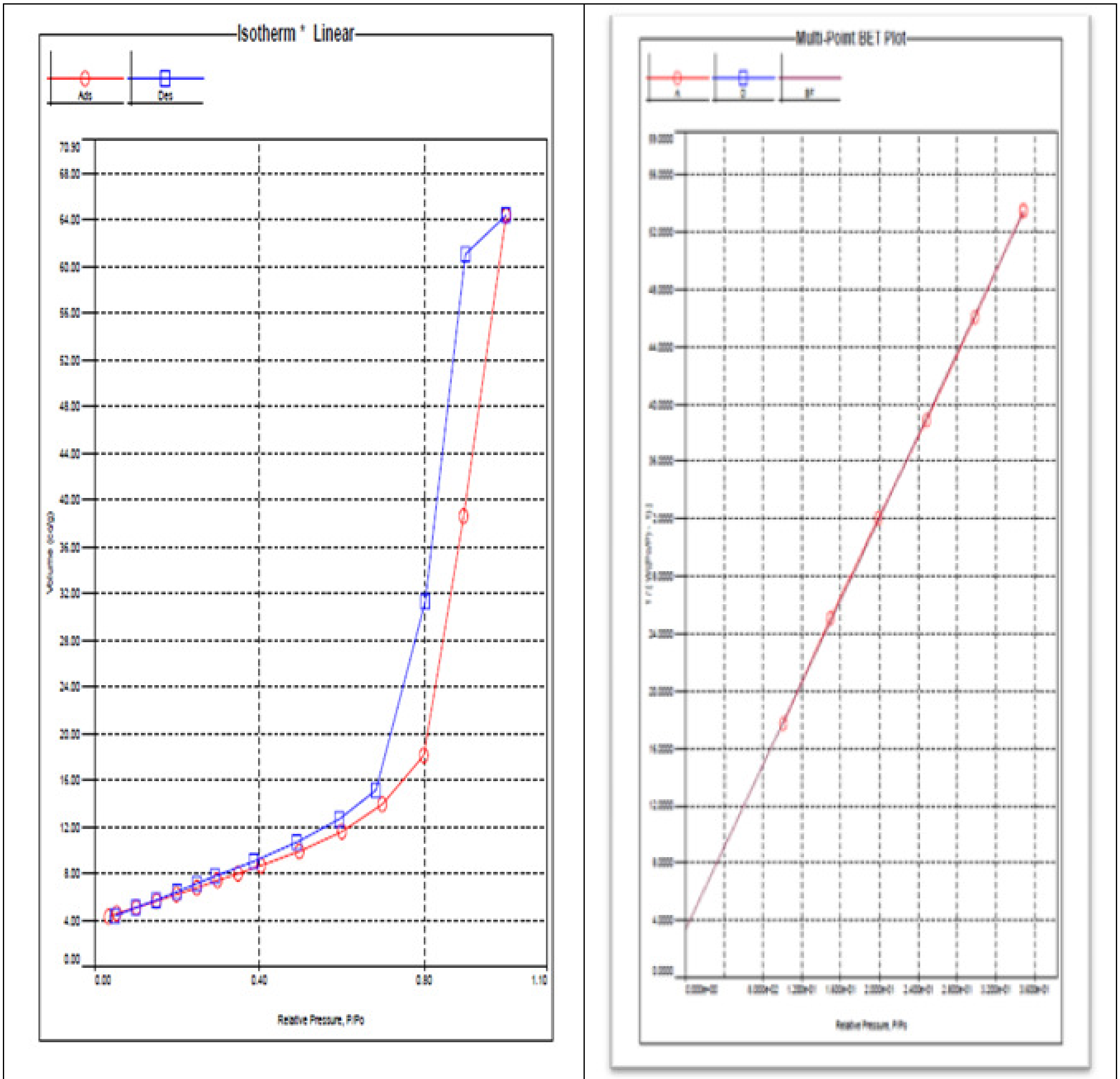
400°C

Figure 4A



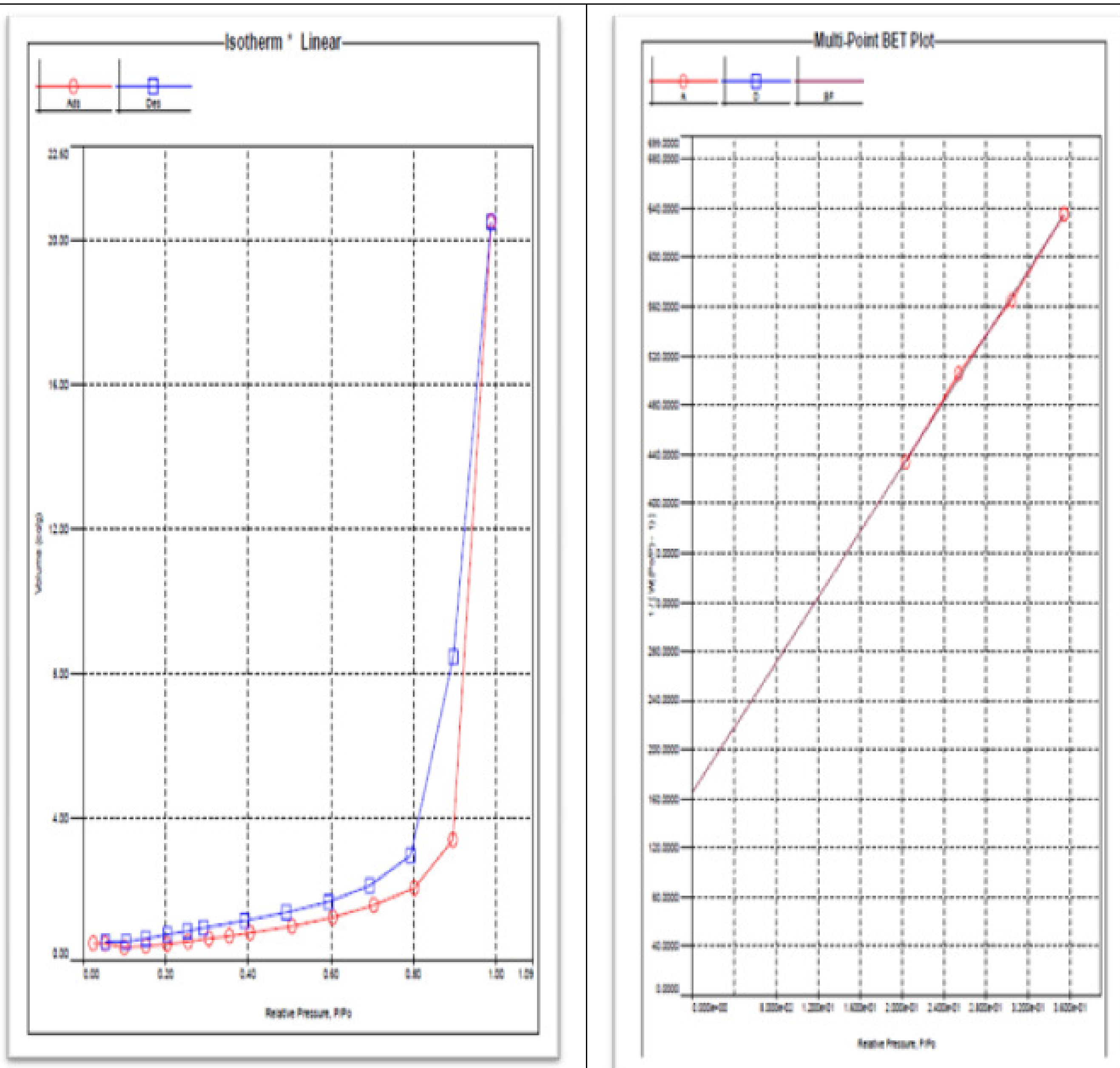
500°C

Figure 4B



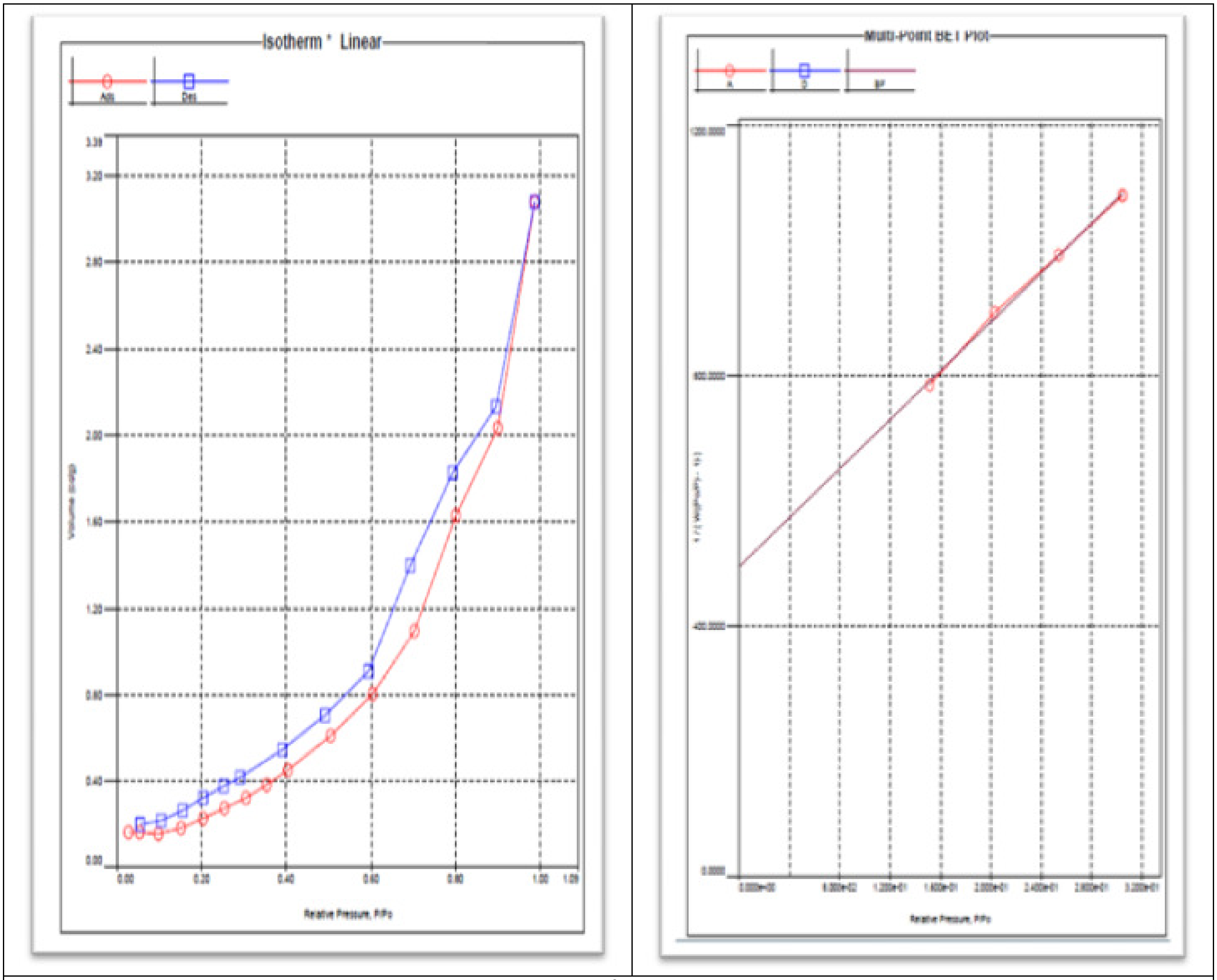
600°C

Figure 4C



700°C

Figure 4D



800°C

Figure 4E: surface area and pore volume of TiO_2 nanoparticles at temperature a(400°C), b(500°C), c (600 °C), d(700°C), e (800 °C)

4. Conclusion

In this work a modification of TiO_2 nanoparticlessynthesized by the sol- gel method, from characterization techniques, that the calcination temperature has a significant impact on the crystal structure of TiO_2 with increasing temperature got the larger crystallite size at 600°C anatase to rutile phase transformation. The particle size increase with increasing calcination temperature at 500°C, the structure was difficult to be seen and became smaller than that at 500°C.Surface area and pore volume decreased with increasing calcination temperature.

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