

(19) **DANMARK**



Patent- og
Varemærkestyrelsen

(10) **DK/EP 2588232 T3**

(12) Oversættelse af
europæisk patentskrift

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- (51) Int.Cl.: **B 01 J 23/22 (2006.01)** **B 01 D 53/94 (2006.01)** **B 01 J 21/06 (2006.01)**
B 01 J 23/30 (2006.01) **B 01 J 35/00 (2006.01)** **B 01 J 35/10 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2020-08-10**
- (80) Dato for Den Europæiske Patentmyndigheds
bekendtgørelse om meddelelse af patentet: **2020-06-17**
- (86) Europæisk ansøgning nr.: **11761486.7**
- (86) Europæisk indleveringsdag: **2011-06-25**
- (87) Den europæiske ansøgnings publiceringsdag: **2013-05-08**
- (86) International ansøgning nr.: **DE2011075149**
- (87) Internationalt publikationsnr.: **WO2012022328**
- (30) Prioritet: **2010-06-29 DE 102010030684**
- (84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV
MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
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- (54) Benævnelse: **Katalysatormateriale og fremgangsmåde til fremstilling heraf**
- (56) Fremdragne publikationer:
US-A1- 2006 084 569
US-B1- 6 380 128

Description

The invention relates to a catalyst material, more precisely a catalyst material based on TiO_2 having a content of metal oxides and/or metal oxide precursors, a
5 process for the production thereof and the use thereof for the removal of pollutants, in particular nitrogen oxides, from combustion gases.

Nitrogen oxides formed in combustion lead to irritation and damage to the respiratory organs (especially in the case of nitrogen dioxide), and formation of
10 acid rain due to formation of nitric acid. In the removal of nitrogen oxides from flue gas (also known as DeNO_x), nitrogen oxides such as nitrogen monoxide (NO) and nitrogen oxides (NO_x) are, for example, removed from the offgas of coal-fired or gas turbine power stations.

15 As measures for removing nitrogen oxides from the offgases, reductive processes such as selective catalytic processes (selective catalytic reduction, SCR) are known in the prior art. The term SCR refers to the technique of selective catalytic reduction of nitrogen oxides in offgases from firing plants, domestic waste incineration plants, gas turbines, industrial plants and engines.

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Many such catalysts contain TiO_2 , with the TiO_2 acting as catalyst itself or acting as cocatalyst in combination with transition metal oxides or noble metals. The chemical reaction over the SCR catalyst is selective, i.e. the nitrogen oxides (NO, NO₂) are preferentially reduced while undesirable secondary reactions (for
25 example the oxidation of sulfur dioxide to sulfur trioxide) are largely suppressed.

There are two types of catalysts for the SCR reaction. One type consists essentially of titanium dioxide, vanadium pentoxide and tungsten oxide. The other type is based on a zeolite structure. Further metal components are also added to
30 the two systems in the prior art.

In the case of TiO_2 - WO_3 - V_2O_5 catalysts, the V_2O_5 serves primarily as catalytically active species on WO_3 -coated TiO_2 (in the anatase modification). The WO_3

coating on the TiO_2 is intended to function as barrier layer to prevent diffusion of vanadium into the TiO_2 and the associated decrease in activity and formation of rutile.

- 5 WO_3 -doped TiO_2 is proposed for catalytic applications, including as DeNO_x catalyst, according to the prior art as per US 4085193. The process known therefrom is based on the addition of tungsten components to a titanium component such as metatitanic acid, a titanium oxyhydrate or titanium dioxide suspension) and subsequent calcination to set the surface area to about 100 m²/g.

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However, an additional, complicated milling step is often required before the further processing of the catalyst raw material. This is due to the fact that the tungsten-containing titanium dioxide material leaving the calcination furnace or after the heat treatment in the range from 150°C to 800°C is in the form of
15 agglomerates in which the individual particles are joined to one another by sintering bridges or similar connections. In the case of relatively high-quality catalysts, in particular catalyst honeycombs having a very low web thickness, or application of the tungsten-containing titanium dioxide in the case of a "washcoat" to honeycomb bodies, milling is indispensable.

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In industry, this milling process is usually carried out in a pendulum mill, e.g. a Raymond mill.

DE 102008033093 describes a process for producing a catalyst material
25 comprising an optionally tungsten-containing titanium dioxide material, in which a titanium dioxide-containing catalyst material is produced as intermediate by milling in a roll mill, in particular a Gutbett roll mill, and the flakes leaving the roll mill as intermediate are not subjected after milling, in particular immediately afterward, to any deagglomeration and/or dispersing treatment.

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The porosity of the catalyst is also of critical importance to the catalytic activity of a titanium dioxide-containing catalyst for the selective removal of nitrogen oxides from exhaust gases and offgases in the presence of ammonia. Thus, EP 516262

describes a shaped porous support composed of titanium dioxide particles alone or of a mixture of titanium dioxide particles with particles of another, porous, inorganic oxide, where the shaped support has a total porosity of $0.8 \text{ cm}^3/\text{cm}^3$ which is made up of a microporosity encompassing pores having a pore diameter of 60 nm or less of from 0.05 to $0.5 \text{ cm}^3/\text{cm}^3$ and a macroporosity encompassing pores having diameters greater than 60 nm of from 0.05 to $0.5 \text{ cm}^3/\text{cm}^3$. This catalyst support is preferably produced by mixing of materials which can be burnt out with titanium dioxide particles and shaping this mixture.

10 US2006/084569A1 discloses a catalyst consisting of titanium oxide, vanadium oxide and a supported metal oxide, wherein the supported metal oxide is selected from the group consisting of oxides of tungsten, molybdenum, chromium, scandium, yttrium, lanthanum, zirconium, hafnium, niobium, tantalum, iron, ruthenium, manganese and mixtures thereof, said supported metal oxide being
15 supported on said titanium oxide thereby forming a titanium oxide supported metal oxide, said catalyst being formed by deposition of said vanadium oxide on said titanium oxide supported metal oxide.

US6380128B1 discloses a V_2O_5 -based catalyst for decomposing nitrogen oxides
20 comprising vanadium pentoxide and one of barium oxide and calcium oxide as active components loaded on a titania support, wherein the titania support is prepared by sufficiently drying and calcining a metatitanate ($\text{TiO}(\text{OH})_2$)-preponderant slurry obtained in the preparation of titania as pigments from ilmenite, and wherein the vanadium pentoxide is present in an amount of about 1.0
25 wt.% to about 10 % by weight based on a total weight of the catalyst, provided that the amount of vanadium pentoxide loaded on the titania support does not exceed about 0.145 grams per square meter of a specific surface area of the titania support.

30 The object of the invention is thus to provide a catalyst material which displays improved properties compared to the materials known in the prior art.

The object is achieved by provision of a catalyst material based on TiO_2 in particle form having a content of metal oxide selected from among vanadium oxide and tungsten oxide and/or precursors thereof, wherein the average particle size D50 after dispersing is $D50 < 1.0 \mu\text{m}$, the size of the mesopores is 3 – 50nm and the
5 volume of the mesopores (mesopore volume) of the particles is greater than $0.260 \text{ cm}^3/\text{g}$.

To determine the mesopore volume, the method of N_2 porosimetry is carried out. The principle is described further below.

10

To determine the average particle sizes D50 after dispersing, the pulverulent catalyst material is dispersed in water by means of an ultrasonic probe (at maximum power, manufacturer: Branson Sonifier 450, use of an increase in amplitude by means of a Booster Horn “Gold”, 1/2” titanium tube having an
15 exchangeable, flat working tip) for 5 minutes. The particle size determination is carried out by means of laser light scattering. Here, the average particle size D50 reported is the D50 median of the volume distribution in percent by volume.

Compared to the materials known from the prior art, the catalyst material
20 according to the invention has a higher mesopore volume, which leads to a higher catalytic activity. Furthermore, the catalyst material of the invention in the form of a tungsten-containing and/or vanadium-containing titanium dioxide displays very good dispersibility and an optimized pore distribution.

25 Such a tungsten-containing titanium dioxide which even as powder, e.g. before application, has an optimized pore distribution is not known in the prior art.

In a further embodiment of the catalyst material, 90% of the particles have a particle size of less than $1.5 \mu\text{m}$ and the average particle size (D50 median of the
30 volume distribution in percent by volume, in each case determined by laser light scattering) is less than $1.0 \mu\text{m}$.

In addition, the pores of the preferably tungsten-containing catalyst material of the invention surprisingly have a bimodal mesopore distribution having maxima in the range from 8 to 12 nm and in the range from 15 to 20 nm. The materials known from the prior art, on the other hand, generally have an approximately monomodal mesopore distribution having a main maximum at from 4 to 7 nm. The invention therefore also provides catalyst materials according to the invention based on TiO_2 having a bimodal mesopore distribution having a maximum in the range from 8 to 12 nm and a further maximum in the range from 15 to 20 nm.

10 In the description of the invention, the definition of pore sizes routine in the literature is as described, for example, in "Fundamentals of Industrial Catalytic Processes", R.J. Farrauto, C. H. Bartholomew, Blackie Academic & Professional, 1997, page 78. This document defines pores having diameters of $d_{\text{Pore}} > 50 \text{ nm}$ as macropores, pores having $d_{\text{Pore}} = 3\text{-}50 \text{ nm}$ as mesopores and pores having
15 $d_{\text{Pore}} < 3 \text{ nm}$ as micropores.

The pore size distribution itself influences the shape selectivity and more rapid diffusion of the gas into and from the particles as a result of larger pore radii is made possible. This leads at the same time to a lower tendency for blockage of
20 the pores as a result of the greater pore radii. In addition, the additional impregnation of the porous, tungsten-containing titanium dioxide with further active metal oxides (e.g. vanadium oxide) is aided by greater pore radii and a greater part of the surface area can therefore be coated with vanadium oxide and is therefore catalytically active.

25 To apply a, for example, tungsten-containing titanium dioxide in the form of a washcoat, the titanium dioxide is dispersed in water. The pH of the suspension is usually set to pH values of < 7 . The titanium dioxide is preferably milled until a defined particle size has been reached. For the purposes of the present invention,
30 good dispersibility means that the particle size after milling is $d_{50} < 1 \mu\text{m}$, preferably $d_{50} < 0.8 \mu\text{m}$.

The particle size distribution of the (e.g. tungsten-containing) titanium dioxide in the washcoat substantially determines the mechanical properties of the finished washcoat, its adhesion to the substrate and the rheological properties of the suspension during the washcoat process. A coarse particle distribution in the washcoat can lead to poor adhesion of the washcoat to the substrate. The production of a readily dispersible (tungsten-containing) titanium dioxide without carrying out a costly milling step is not known in the prior art, but is made possible according to the invention.

As a result of the better dispersibility of the catalyst material of the invention, i.e. the lower particle size after dispersing, the adhesion of the washcoat produced is improved and the accessible surface area is increased.

The inventive catalyst material based on TiO_2 preferably has a content of metal oxide and/or precursors thereof of less than 30% by weight based on the total amount of titanium dioxide and metal compound used. For the purposes of the present invention, precursors thereof are, for example, hydrated forms of oxides, hydroxides, etc., which are transformed thermally into the metal oxides. A metal oxide, in particular WO_3 , in an amount of from 8 to 15% by weight based on the total amount of titanium dioxide and metal oxide or compound used is suitable here. Particular preference is given to the metal oxide or its precursor being introduced into the catalyst material by addition of an ammonium compound such as ammonium tungstate. For the purposes of the invention, metal oxide precursors are, for example, hydrated forms of oxides, hydroxides, etc., which are transformed thermally into the metal oxides.

The inventors have discovered that the specific surface area of the catalyst material of the invention at values of $100 \text{ m}^2/\text{g}$, $200 \text{ m}^2/\text{g}$ and $300 \text{ m}^2/\text{g}$ in each case corresponds to an amount of 15% by weight, 30% by weight and 45% by weight of metal oxide, in each case based on the total amount of titanium dioxide and metal oxide and/or precursors thereof used. The invention therefore also provides catalyst materials having a content of up to 15 or 45% by weight and the corresponding specific surface area in each case.

The catalyst material of the invention can be obtained by a process in which a suspension having a content of metatitanic acid $\text{TiO}(\text{OH})_2$ of preferably from 200 to 400 g of TiO_2/l is initially charged, the suspension is brought to a pH in the range from 3 to 8 and, after a ripening time, preferably in a temperature range from 60 to 100°C for a period of up to 180 minutes, is subjected to a hydrothermal treatment, preferably in the temperature range from 150 to 300°C for a period of up to 24 hours, the suspension obtained is washed and filtered and the particulate material filtered off is dried, with a soluble compound of the metal being added to the suspension during the course of the process.

The addition of the soluble metal compound can be carried out before or after the hydrothermal treatment, and addition before setting of the pH to the range from 3 to 8 is also possible. The addition of the soluble metal compound preferably takes place after the pH adjustment before the hydrothermal treatment. However, it is also possible to carry out the addition of the metal compound in a plurality of steps, i.e. to add partial amounts both before and after the hydrothermal treatment.

As soluble metal compound, it is possible to use a compound which is transformed thermally into a catalytically active metal oxide and/or metal oxide precursor, e.g. into SnO_2 , CeO_2 , VO_x , CrO_x , MoO_x , WO_x , MnO_x , FeO_x and NiO and CoO_x . According to the invention, particular preference is given to adding a vanadium compound and/or tungsten compound, preferably in the form of a vanadate or tungstate. Very particular preference is given to the use of ammonium metatungstate.

The setting of the pH can, according to the invention, be carried out using any neutralizing agent, but preference is given to the use of ammonia since, in particular, the introduction of alkali metal ions is avoided.

Phosphoric acid can optionally be added before setting of the pH. This increases the thermal stability of the end product.

Ammonium sulfate can optionally be added after the hydrothermal treatment. This makes targeted setting of the sulfate content possible. This makes it possible for the thermal stability and the catalytic activity to be increased further.

- 5 The invention thus makes it possible to overcome the disadvantages of the materials of the prior art and, in particular, to provide a process for producing a TiO₂-containing catalyst material which leads to catalyst materials based on TiO₂ in the anatase form, with the catalyst material having good dispersibility and a bimodal mesopore distribution.

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In the opinion of the inventors, this is made possible essentially by the use of the hydrothermal process. Here, unlike in the case of ignition, the TiO₂ (present as titanium oxide hydrate) is introduced after filtration and washing and setting of the pH of the suspension to pH 3-8 into a pressure vessel (autoclave) and maintained
15 at temperatures of > 100°C for a period of from one hour to a plurality of (e.g. 5) days. This process step is referred to as hydrothermal treatment (cf. also Ullmanns Enzyklopädie der Technischen Chemie, 4th edition, 1978, Volume 15, p. 117ff: K. Recker, growing single crystals). A preferred period of time for the hydrothermal treatment of the TiO₂ (present as titanium oxide hydrate) is from 2 to 24 hours,
20 particularly preferably from 4 to 8 hours. In this way, more homogeneous crystal growth can be achieved in the aqueous suspension by the hydrothermal treatment with stirring, since in contrast to calcination no "hot spots" occur.

The catalyst material which can be obtained by the process of the invention can,
25 particularly as dried material, be used further directly and generally does not have to be subjected to milling.

The process of the invention can therefore, in summary, provide the following process steps:

- 30
- initial charging of the starting material in the form of a titanium oxide hydrate suspension
 - optional addition of phosphoric acid

- optional addition of a preferably water-soluble metal compound, in particular a tungsten compound (very particularly preferably ammonium metatungstate)
- adjustment of the pH to pH 3-8 (in particular with the aid of ammonia)
- 5 - optional addition of a preferably water-soluble metal compound, in particular a tungsten compound (very particularly preferably ammonium metatungstate)
- ripening time
- hydrothermal treatment
- 10 - filtration and washing
- optional addition of ammonium sulfate
- optional addition of a preferably water-soluble metal compound, in particular a tungsten compound (very particularly preferably ammonium metatungstate)
- 15 - drying (preferably spray drying or milling-drying)
- optional milling.

The addition of the metal compound, in particular a tungsten compound, is possible according to the invention in various process stages. Thus, partial
20 amounts of the total amount of tungsten component can be added in various process stages, e.g. before setting of the pH and before the hydrothermal treatment. It has surprisingly been found that a catalyst material produced in this way has good dispersibility and a bimodal mesopore distribution.

25 The invention is illustrated with the aid of the following experiments and comparative experiments and also figures 1-8.

Production examples according to the invention

As starting materials the following materials were used:

Materials	Remarks	Concentration
Titanium oxide hydrate suspension	TiO(OH) ₂ or TiO ₂ in the anatase modification	358 g of TiO ₂ /l
Ammonium metatungstate soln. (AMT)	prepared from AMT (H.C. Starck, Lot. AMW01706) containing 91.36% of WO ₃ , dissolved at RT	39.4% of WO ₃
Phosphoric acid	AR grade, from Merck	89% strength, ρ = 1.75 g/ml
Ammonia	AR grade, from Merck	25% strength

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Production example 1

5.6 l of the abovementioned titanium oxide hydrate suspension were introduced into a 10 l glass beaker and diluted with 1067 g of TE water. The mixture was heated to 60°C while stirring. The pH was set to pH = 8.0 by addition of aqueous ammonia solution. About 5800 ml of suspension were placed in a 10 l pressure vessel. The suspension was HT-treated at about 180°C and 10 bar for 4 hours. After cooling overnight, the suspension was still at about 65°C. The suspension was filtered. The solid was washed with about 8 l/kg of TiO₂ (≙ 13.1 l) of TE water. The filtercake was slurried with TE water and the suspension was admixed with 476 g of AMT solution while stirring. Since the suspension thickened during the addition, it was diluted to about 7 l with TE water. The suspension was spray dried. The results are given in table 1 below.

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Production example 2

5.6 l of the abovementioned titanium oxide hydrate suspension were introduced into a 10 l glass beaker and diluted with 1067 g of TE water. The pH was then set to pH = 3.0 by means of aqueous ammonia solution. The mixture was heated to 60°C while stirring and firstly maintained at this temperature for 1 hour. 828 g of

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AMT solution were subsequently added. About 5800 ml of suspension were placed in a 10 l pressure vessel. The suspension was HT-treated at about 180°C and 10 bar for 4 hours. After cooling overnight, the suspension was still at about 65°C. The suspension was filtered. The solid was washed with about 6 l/kg of TiO₂ (± 10 l) of TE water. The filtercake was slurried with TE water to about 5 l and the suspension was spray dried.

Production example 3

5.6 l of the abovementioned titanium oxide hydrate suspension were introduced into a 10 l glass beaker and diluted with 1067 g of TE water. 16 ml of phosphoric acid were added (pH 1.8). The mixture was heated to 60°C while stirring (pH 1.4). 354 ml of ammonia were then added over a period of about 24 minutes (15 ml/min) to the suspension in order to set the pH to 5.0. About 5800 ml of suspension were placed in a 10 l pressure vessel. The suspension was HT-treated at about 180°C and 10 bar for 4 hours. After cooling over the weekend, the suspension was still at about 25°C. The suspension was filtered. The solid was washed with about 6 l/kg of TiO₂ (± 10 l) of TE water. The filtercake was slurried with TE water and the suspension was admixed with 476 g of AMT solution while stirring. Since the suspension thickened during the addition, it was diluted to about 7 l with TE water. The suspension was spray dried.

Production example 4

1955 ml of the abovementioned titanium oxide hydrate suspension were introduced into a 10 l glass beaker and diluted with 5045 g of TE water. 5.6 ml of phosphoric acid were added (pH 1.8). The mixture was heated to 60°C while stirring (pH 1.7). 125 ml of ammonia were then added over a period of about 8 minutes (15 ml/min) to the suspension to set the pH to 6.9. About 5600 ml of suspension were placed in a 10 l pressure vessel. The suspension was HT-treated at about 180°C and 10 bar for 4 hours. After cooling overnight, the suspension was still at about 60°C. The solid was washed with about 2 l/kg of TiO₂ (± 1.1 l) of TE water. The filtercake was slurried with TE water and the suspension was admixed with 164 g of AMT solution while stirring. Since the suspension thickened

during the addition, it was diluted to about 3.5 l with TE water. The suspension was spray dried.

Table 1 shows the analyses of the products of production examples 1 to 4 and the determination of the surface area, the pore size and the thermal stability.

Table 1 – Production examples 1 to 4					
	Process	1	3	2	4
Pore volume	N ₂ Ads./ Total	0.350 cm ³ /g	0.276 cm ³ /g	0.300 cm ³ /g	0.294 cm ³ /g
Mesopore volume	N ₂ Ads./ BJH	0.340 cm ³ /g	0.274 cm ³ /g	0.297 cm ³ /g	0.293 cm ³ /g
Pore diameter	N ₂ Ads./ BJH Des.	8.1 to > 15.6 nm*	11.5 to > 19.3 nm*	9.0 to > 19.2 nm*	9,0 to > 19.3 nm*
Spec. surface area of end product		128 m ²	73.9 m ²	88.6 m ²	83.4 m ²
d50 Helos UF		0.68 µm	0.46 µm	0.51 µm	0.47 µm
B90/10 Helos UF		0.94 µm	0.78 µm	0.83 µm	0.80 µm

To determine the mesopore volume, the method of N₂ porosimetry is carried out, as mentioned above. The principle is described, for example, in “Fundamentals of Industrial Catalytic Processes”, R.J. Farrauto, C. H. Bartholomew, Blackie Academic & Professional, 1997, page 122. For the sample preparation, the samples were dried under defined conditions (16 hours under reduced pressure and 1 hour under reduced pressure at T = 180°C). For the measurement, use is made of, for example, the measuring instrument “Autosorb-6” from Quantachrome.

To determine the mesopore volume, the evaluation by the BJH method (as per Barret, Joyner and Halenda) is carried out.

The pore distribution of the materials produced in production examples 1 to 4 is shown in the accompanying figures 1 to 4.

Comparative experiments

In the same way as in the production examples according to the invention, the suspensions of titanium oxide hydrate were made up in the comparable concentrations for comparative experiments 1 to 4 and treated as indicated in
5 table 2 below. As starting materials, use was made of the following materials:

Materials	Remarks	Concentration
Titanium oxide hydrate suspension	TiO(OH) ₂ or TiO ₂ in the anatase modification	386 g of TiO ₂ /l
Ammonium metatungstate soln. (AMT)	prepared from AMT (H.C. Starck, Lot. AMW01706) containing 91.36% of WO ₃ , dissolved at RT	40% of WO ₃
Phosphoric acid	AR grade, from Merck	89% strength ρ = 1.75 g/ml
Ammonia	AR grade, from Merck	25% strength

Comparative example 1

1815 ml of the abovementioned titanium oxide hydrate suspension were
10 introduced into a 5 l glass beaker and diluted with 1815 ml of water. A pH of 1.7 was measured. The pH was set to 6.8 by means of ammonia while stirring. The mixture was stirred at RT for 2 hours. The suspension was filtered with suction and the solid was washed with 5.6 l of TE water (= 8 l/kg of TiO₂). The filtercake (1810.4 g = 38.67% of TiO₂) was divided. 776.0 g of filtercake were dispersed in
15 TE water by means of a high-speed mixer and diluted to about 1.5 l. The 83.25 g of AMT solution were added dropwise over a period of 15 minutes while stirring. The mixture was stirred for a further 1 hour at RT. The suspension was introduced into a porcelain dish. Tray drying at 150°C was carried out overnight. Ignition at 460°C was carried out. The product was milled.

20

Comparative example 2

The remaining filtercake from comparative example 1 was dried overnight at 150°C in a drying oven, ground in a mortar and divided into two halves. One half was mixed with 55.6 g of AMT solution. Ignition was carried out at 460°C in a Nabertherm furnace. The product was milled.

5

Comparative example 3

The second half from comparative example 2 was calcined at 460°C in a Nabertherm furnace. It was then mixed with 55.6 g of AMT solution. The product was milled.

10

Comparative example 4

The after-treatment was carried out in a 5 l laboratory reactor. For this purpose, 1500 ml of the abovementioned titanium oxide hydrate suspension were introduced into the product vessel and diluted with 1500 ml of water.

15 After-treatment conditions:

Temperature before and during

AMT addition: 80 °C

AMT addition: over a period of 20 minutes (160.8 g)

Temperature after AMT addition: boiling point

20 Ripening: 2 h at boiling point

H₃PO₄ addition: after ripening at about 90°C (6.17 g)

Further stirring after H₃PO₄ addition: about 30 minutes with cooling to about 40°C

pH of the suspension: 1.0

25 The suspension was filtered with suction. The filtercake was tray dried at 150°C. The product was ignited at 460°C and subsequently milled using a Braunmix milling attachment.

Table 2 – Comparative experiments 1 to 4					
Expt. No.		1	2	3	4
Pore volume	N2 Ads./Total	0.254 cm³/g*	0.225 cm³/g*	0.198 cm³/g*	0.246 cm³/g*
Mesopore volume	N₂ Ads./BJH	0.250 cm³/g*	0.216 cm³/g*	0.191 cm³/g*	0.225 cm³/g*
Pore diameter	N₂ Ads./average	9.2 nm	7.6 nm	9.6 nm	6.7 nm
Pore diameter	N₂ Ads./BJH Des.	5.1 to >50 nm	4.4 to > 50 nm	6.3 to > 50 nm	3.8 to > 50 nm
Spec. surface area of end product	N₂ Ads./5P-BET	111 m²/g	119 m²/g	82.7 m²/g	146 m²/g
d50 Helos UF		1.03 µm	1.05 µm	1.03 µm	1.01 µm
B90/10 Helos UF		1.54 µm	1.60 µm	1.53 µm	1.52 µm

The pore distribution of the materials produced in comparative examples 1 to 4 is shown in the accompanying figures 5 to 8.

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As can be seen from a comparison of the results of the production examples and the comparative examples, the materials according to the invention have improved properties in respect of particle diameter, pore size and pore diameter compared to materials produced according to the prior art.

10

P a t e n t k r a v

- 5 **1.** Katalysatormateriale på TiO_2 -basis i partikelform med et indhold af metaloxid, udvalgt fra vanadiumoxid og wolframoxid, og/eller fortrin deraf, hvor middelpartikelstørrelsen D_{50} efter dispergering er $D_{50} < 1,0 \mu\text{m}$, størrelsen af mesoporerne er 3-50 nm, og volumen af partiklernes mesoporer er mere end $0,260 \text{ cm}^3/\text{g}$.
- 10 **2.** Katalysatormateriale på TiO_2 -basis ifølge krav 1 med et indhold af metaloxid og/eller fortrin deraf i en mængde på mindre end 30 vægtprocent baseret på den samlede mængde af anvendt titandioxid og metaloxid.
- 15 **3.** Katalysatormateriale på TiO_2 -basis ifølge krav 1 med et indhold af metaloxid og/eller fortrin deraf, anvendt som wolframat i en mængde på 8 til 15 vægtprocent af den samlede mængde af anvendt titandioxid og metaloxid.
- 20 **4.** Fremgangsmåde til fremstilling af katalysatormaterialet på TiO_2 -basis ifølge et af kravene 1 til 3, hvor en vandig suspension med et indhold af titanoxidhydrat $\text{TiO}(\text{OH})_2$ på fortrinsvis 200 til 400 g TiO_2 / L frembringes, suspensionen indstilles til en pH-værdi i området fra 3 til 8 og efter en modningstid udsættes for en hydrotermisk behandling, den opnåede suspension vaskes og bortfiltreres, og det bortfiltrerede partikelformede materiale tørres, hvor der til suspensionen i løbet af fremgangsmåden tilsættes en opløselig forbindelse af et metal, udvalgt fra vanadium og wolfram.
- 25 **5.** Fremgangsmåde ifølge krav 4, hvor tilsætningen af den opløselige forbindelse af metallet sker før den hydrotermiske behandling.
- 30 **6.** Fremgangsmåde ifølge krav 5, hvor tilsætningen af den opløselige forbindelse af metallet sker efter indstillingen af pH-værdien til området 3-8 og før den hydrotermiske behandling.

- 7.** Fremgangsmåde ifølge et af kravene 5 eller 6, hvor der som metal tilsættes en vanadium- eller wolframforbindelse, fortrinsvis i form af et vanadat eller wolframmat, især foretrukket ammoniummetawolframmat.
- 5 **8.** Fremgangsmåde ifølge et af kravene 5 til 7, hvor suspensionen indstilles til en pH-værdi i området fra 3 til 8 med ammoniak.
- 10 **9.** Anvendelse af katalysatormaterialet, som er fremstillet i henhold til en fremgangsmåde ifølge kravene 5 til 8, eller katalysatormaterialet på TiO_2 -basis ifølge et af kravene 1 til 3 til fremstilling af en udstødningsgaskatalysator, i kemiske katalyseprocesser eller som fotokatalysator.
- 15 **10.** Anvendelse af katalysatormaterialet, som er fremstillet i henhold til en fremgangsmåde ifølge kravene 5 til 8, eller katalysatormaterialet på TiO_2 -basis ifølge et af kravene 1 til 3 til fjernelse af skadelige stoffer, især af nitrogenoxider i udstødningsgasser.

Figure 1/8

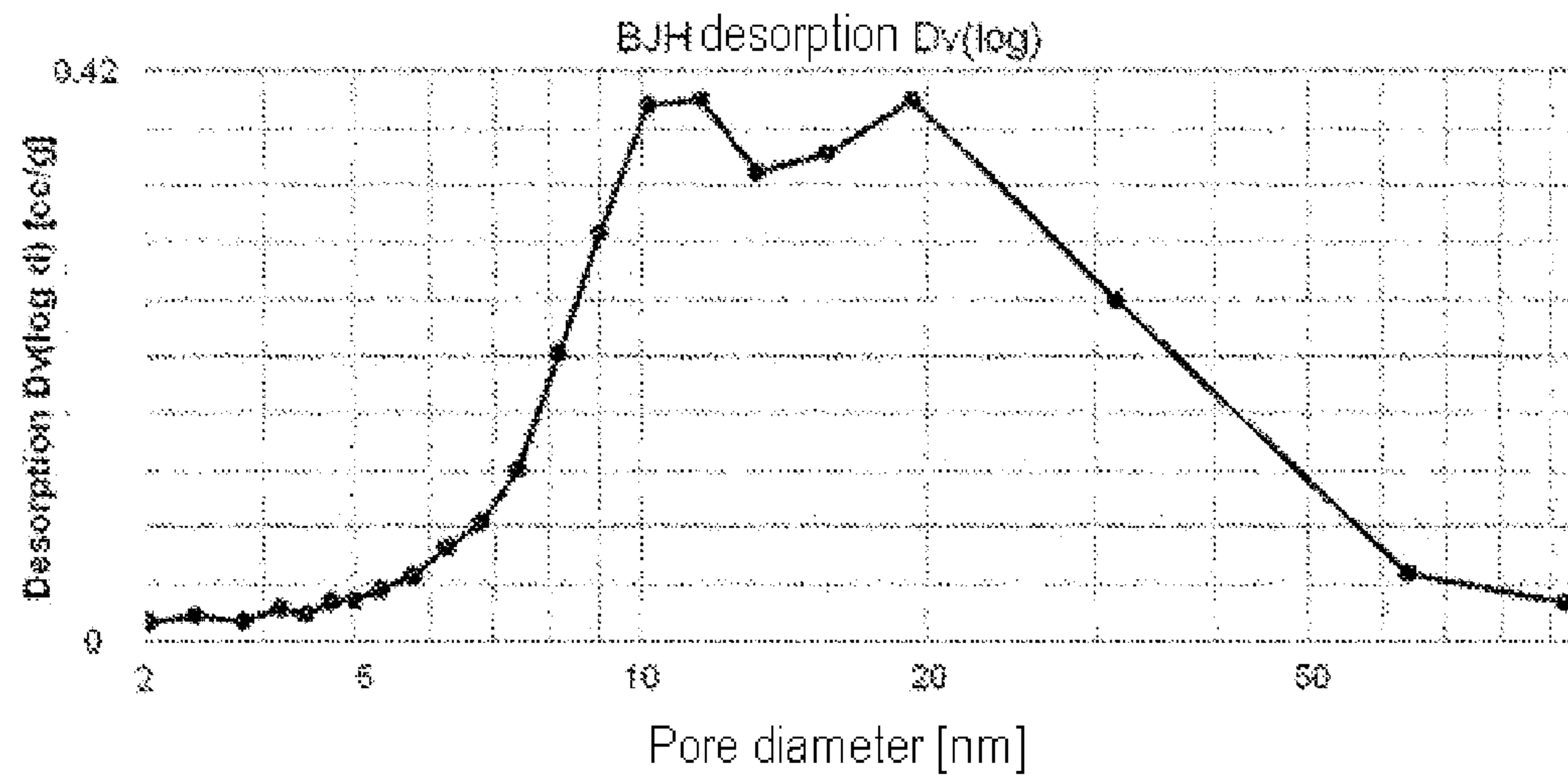


Figure 2/8

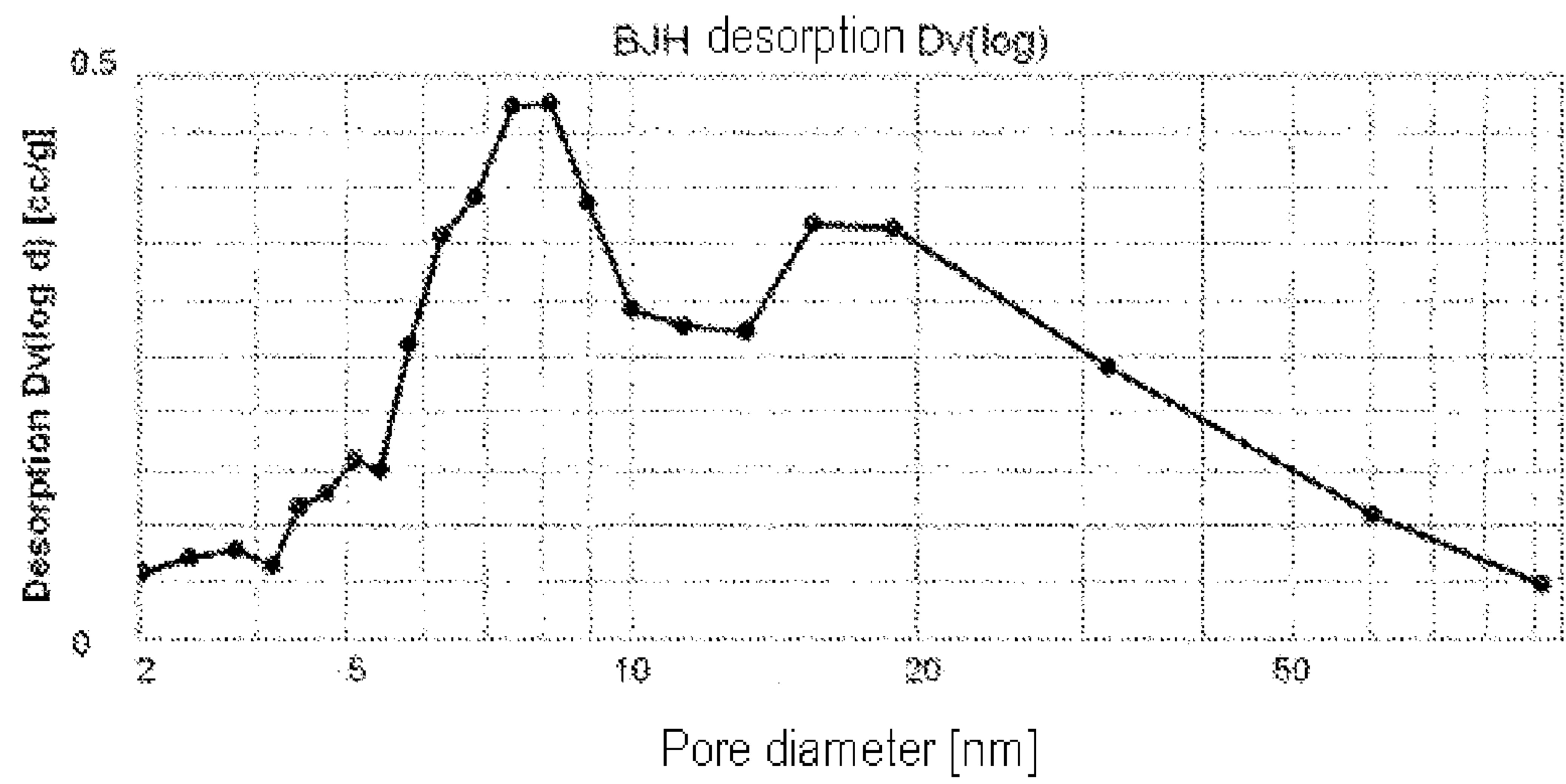


Figure 3/8

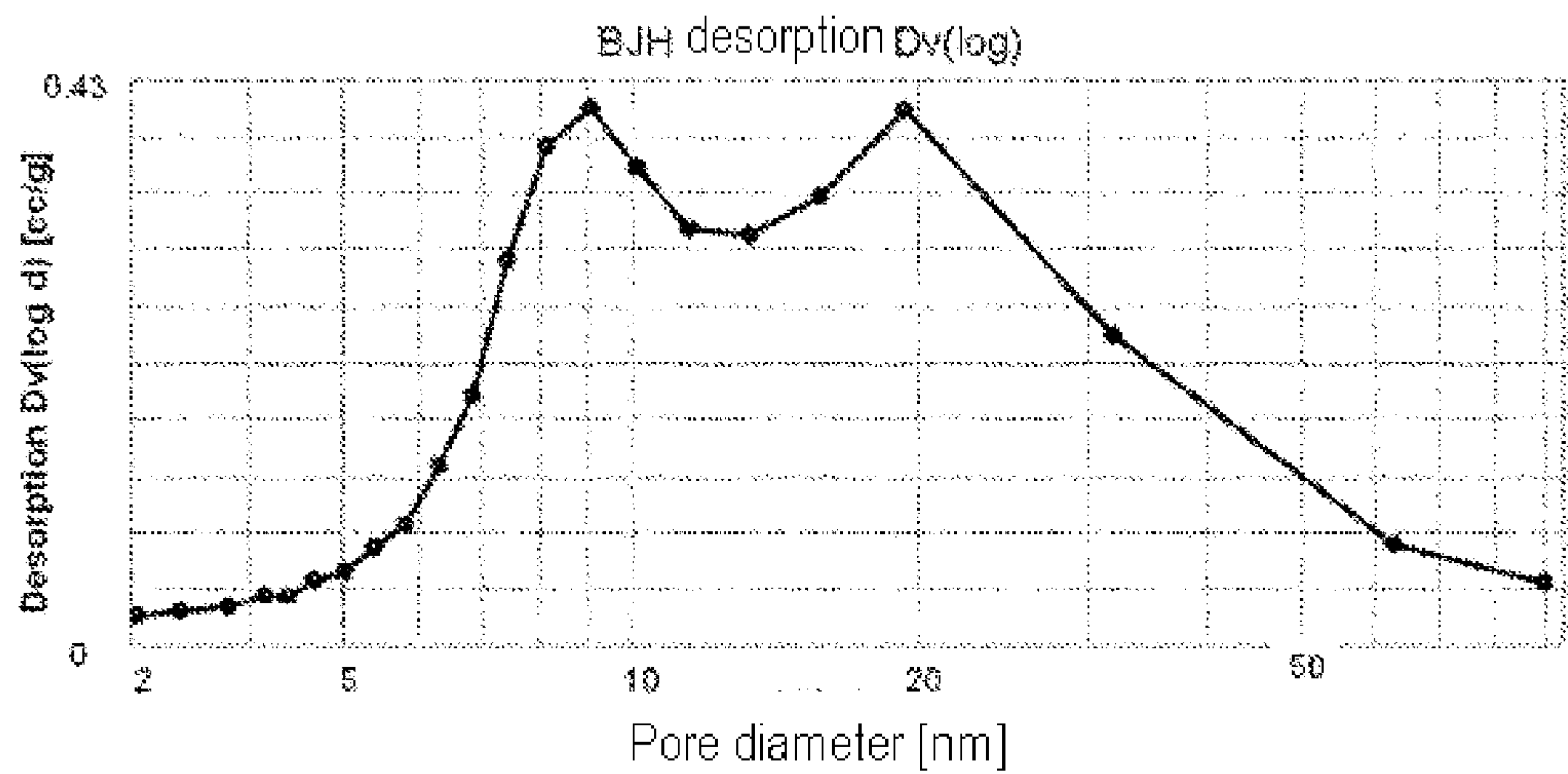


Figure 4/8

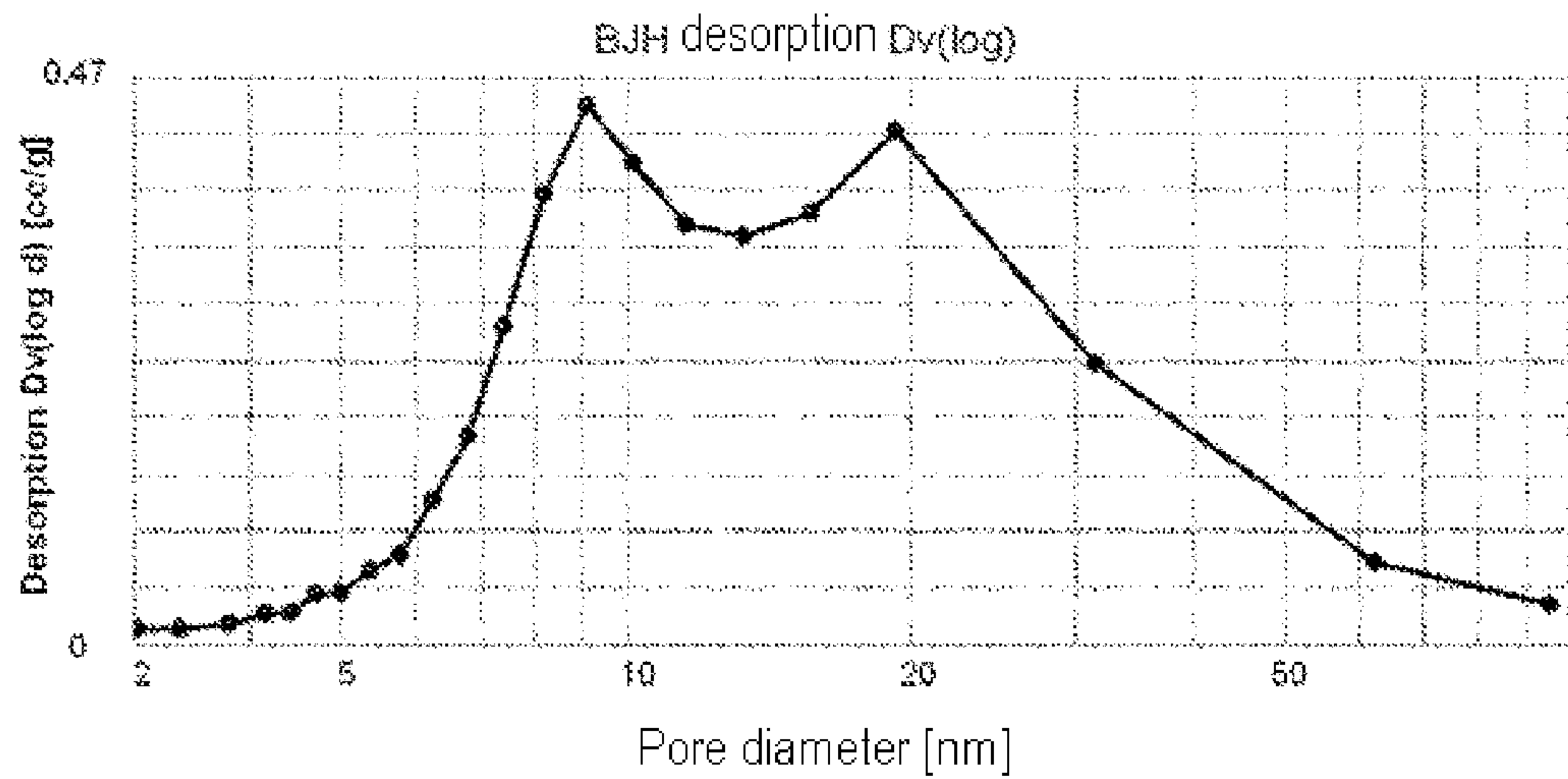


Figure 5/8

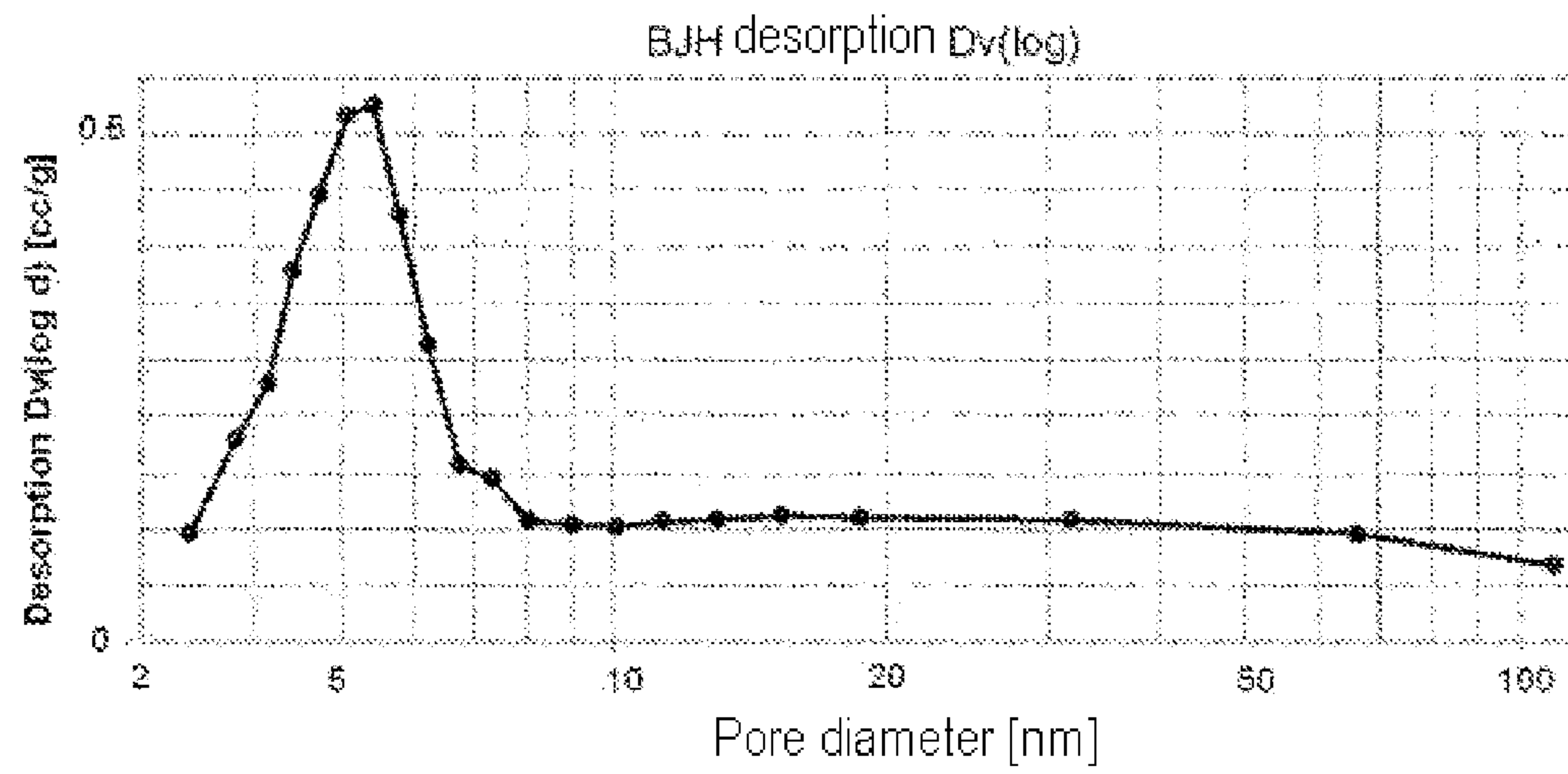


Figure 6/8

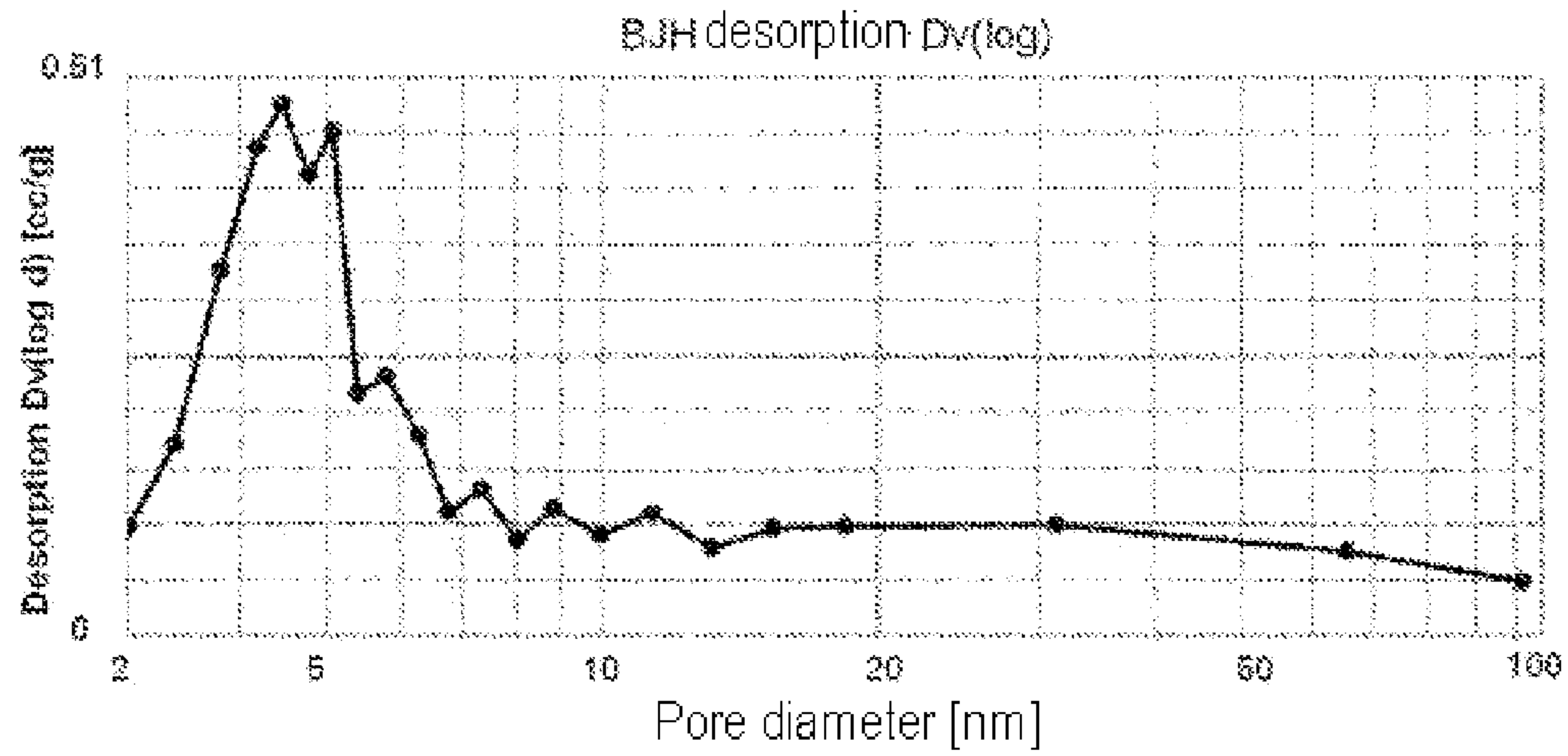


Figure 7/8

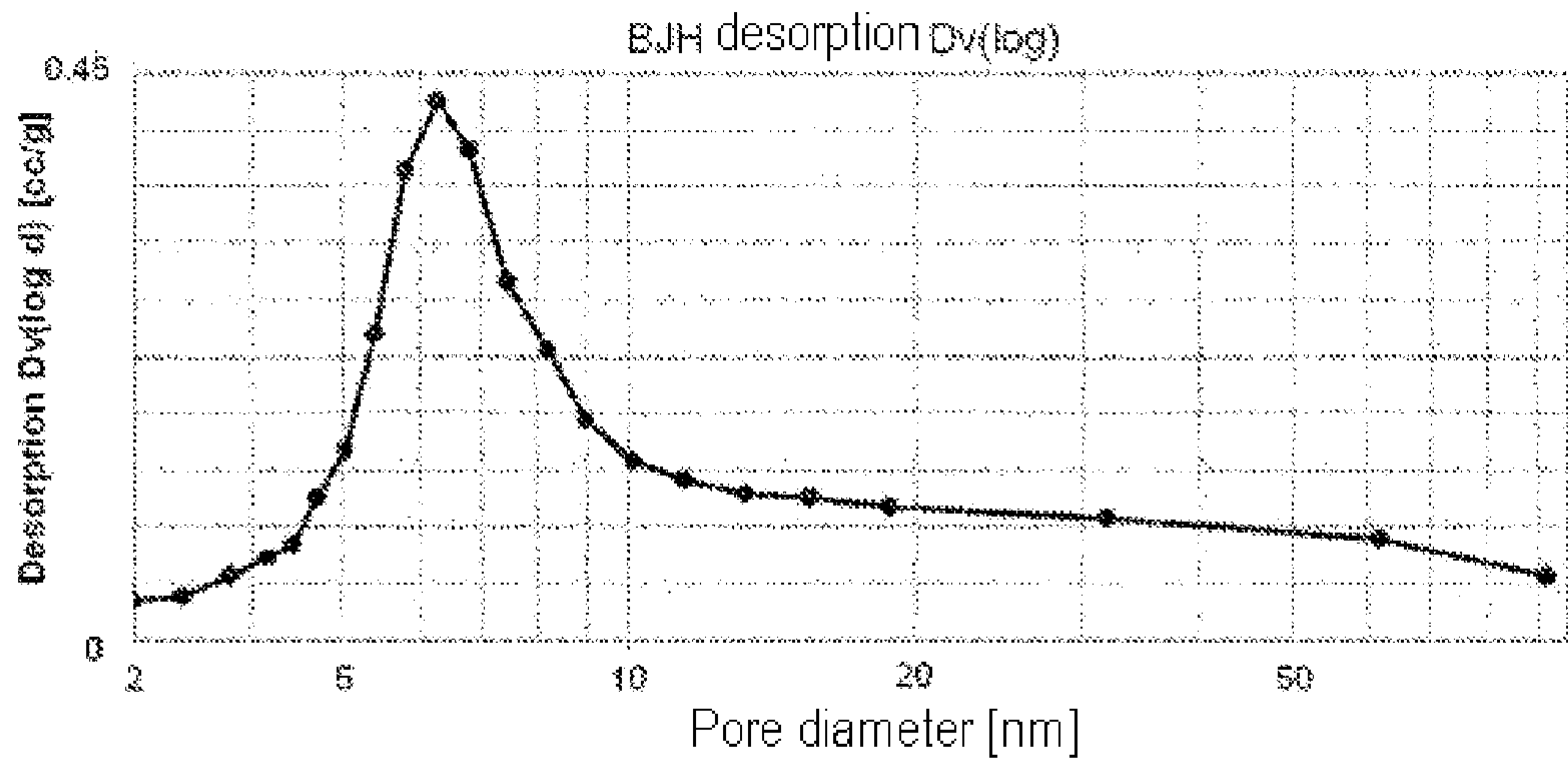


Figure 8/8

