“Photo Catalytic Degradation of concentrated effluent”

A Major Project Report

Submitted in Partial Fulfillment of the Requirements
For the Degree of

MASTER OF TECHNOLOGY

IN

Chemical Engineering
(ENVIRONMETAL PROCESS DESIGN)

By
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2005/2006

A MAJOR PROJECT

CODE: 3CH1301

"Photo Catalytic Degradation of concentrated effluent"

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Certificate

This is to certify that the Major Project Report entitled "**Photo catalytic degradation of concentrated effluent**" submitted by **Mr. Jaxesh. P. Trivedi (04MCH009)**, towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Chemical Engineering (EPD) of Nirma University of Science and Technology is the record of work carried out by him under my supervision and guidance. The work submitted has in my opinion reached a level required for being accepted for examination. The literature embodied in this major project work to the best of my knowledge has not been submitted to any other University or Institution for award of any degree or diploma.

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Abstract:

Many toxic harmful pollutants enter the water bodies, soil and atmosphere directly or indirectly. Industrial wastewater which may contain highly toxic/refractory compounds, needs special treatments before it can be recycled (or even dispose of).Some time these pollutants are not treated with conventional methods. For them we have to go for advance oxidation process. Photo catalytic methods offer some distinct advantage over conventional technologies, such as air stripping, vapor extraction, and carbon adsorption. In this process oxidation occurs through an attack by $^{\cdot}OH$, which has a rate constant billion times higher than normal oxidation rater constants. The treatment of wastewater using this method gives good results.

This project involves photo catalytic degradation of wastewater using titanium dioxide as catalyst. Titanium dioxide has some good advantage which gives the best treatment results for wastewater in combination with UV-light.

Ahmedabad Textile Industry's Research Association, Ahmedabad

(ATIRA)

ATIRA is an autonomous non-profit premiere R&D laboratory for textile research consultancy, testing and training in the textile and allied fields. It is the largest of its kind in India for textile and allied industries. ATIRA was established on 13th December 1947, and started in 1949 after due recognition by the Council of Scientific and Industrial Research under the Ministry of Science and Technology, Government of India. Later it was linked to the Ministry of Textiles. ATIRA is located in Ahmedabad, 900 km South West of New Delhi and 500 km North of Mumbai. It is well connected by air, rail and roads. Other major educational institutions such as Gujarat University, PRL, L.D. Engineering College, IIM and AMA surround the ATIRA campus.

Idea conceived by Shri Kasturbhai Lalbhai, Vikram Sarabhai and Shri S.S. Bhatnagar. The Foundation stone laid by Shri Sardar Vallabhbhai Patel on 1st November 1950. Building Inauguration by Pt. Jawaharlal Nehru on 10th April 1954. The 1st Honorary Director – Dr. Vikram Sarabhai.

ATIRA membership is voluntary of 101 units spread all over India and abroad, 64 are Ginning, Spinning, Weaving, Process Houses and Composite Textile Units and 37 are manufacturers of fibers, dyes, chemicals, instruments, equipments and machinery.

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NOMANCLATURE:

U	Energy of the photon
h	Plank’s constant (($6.626 * 10^{-34}$ J s)
c	Speed of the light, m/sec
λ	Wave length of the molecule
E_λ	Spectral irradiance, $Wm^{-2}\ nm^{-1}$,
α_λ	Absorption coefficient, $cm^{-1}\ atm^{-1}$
pi	Partial pressure of component i
ϵ_λ	Extinction coefficient, $M^{-1}\ cm^{-1}$
c_i	Concentration of component i
COD	Chemical oxygen demand

CHAPTER 1

INTORDUCTION AND OBJECTIVE

1.1 Introduction:

Advance oxidation processes have been broadly defined as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical, as the primary oxidant. The OH radical is among the strongest oxidizing species used in water and wastewater treatment and offers the potential to greatly accelerate the rate of contaminant oxidation. [1]

The generation of OH radicals is commonly accelerated by combining ozone, hydrogen peroxide, titanium dioxide, heterogeneous photo catalysis, uv radiation, ultrasound and high electron beam irradiation. Of these, photo catalytic processes hold the greatest promise to detoxify water and wastewater.

1.2 Aim of the project:

The overall objective of this project is to degrade the waste contaminants which are not easily degrade by conventional methods. We also look to reduce toxicity, odour, and color as well. In order to fulfill this first lab scale experiment is carried out on the basis of literature reviews. Here we are using titanium dioxide as catalyst which is very cheap is cost. Titanium dioxide is treated with selected industrial wastewater and then this is processed with UV light. This will degrade contaminants. Only UV light or titanium dioxide will not degrade wastewater.

This project has been carried out in Ahmedabad Textile Industry's Research Association's ATIRA, Ahmedabad.

1.3 Significance of the Project:

Advance oxidation processes are finding increased application in destruction of water bound organic compounds. AOPs involve the generation of highly reactive radicals the can mineralize organic compounds to non toxic forms such as carbon dioxide and water. The potential advantages of using AOPs that employ heterogeneous reactions are:

- A wide spectrum of organic compound may be mineralized including those that are not amenable to carbon adsorption and air stripping. Additional electron acceptors may not be required.
- The photo catalysis may be recovered and reused.
- Eventually solar radiation may be employed as a light source to activate the catalyst.

1.4 Objective:

The overall objective of this project is to achieve:

- To degrade contaminants which are not easily processed by conventional methods.
- To reduce toxicity
- To reduce color and odor of wastewater
- Try to make it for commercial or pilot scale.

1.5 Scope:

The potential of heterogeneous photo catalysis to mineralize a host of pollutants in water has been now largely established. The method does not require any chemical reactant apart from oxygen or air. Over the next decade, in order to commercialize photocatlysis, researchers need to design reactors that increase the efficiency of photon utilization. The potential for increasing process efficiency by developing more active photo catalyst than those commercially available i.e. the amount of light energy required should be decrease three to four times for the total destruction. There will be market for this type of process since it is an on site treatment which breaks down the waste to non toxic inorganic compounds. [2]

CHAPTER 2

LITERATURE REVIEW

2.1 Catalysis in general:

Catalysts are a big business and the chemical industry depends upon catalysts; People depend upon the chemical industry for our 21st century

- 80 % of processes in chemical industry use catalysts
- Catalyst sales in 2000 were worth 8 to 10 million USD
- Growth in catalyst sales is increasing, between 5 % and 10 % per year
- Turnover in industry using catalysts was about 14 trillion USD,which is equal to the gross domestic product of Italy
- The conversion of non-renewable resources (coal, raw oil, natural gas) uses catalysts

Catalysts can have an enormous impact on the chemical industry and everyday life:

- Enable reactions to take place
- Make processes more efficient
- A 0.5 % to 1 % increase in selectivity can lead up to one million USD increase in operating profile

Figure -2.1 Worldwide Catalyst Markets

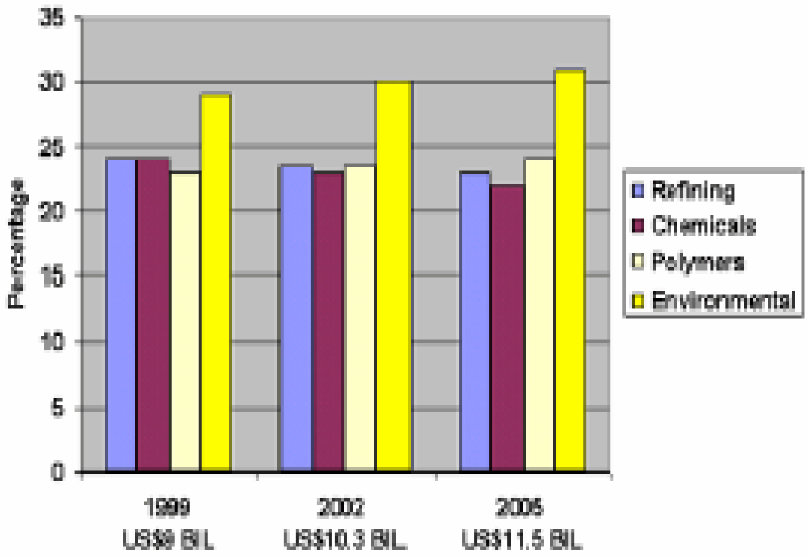


Table - 2.1 Global Catalyst Market (Billion USD)

Sector	1995	1999	2001	2002	2005
Refining	1.9	2.2	2.4	2.4	2.6
Chemical	2.2	2.2	2.5	2.3	2.5
Polymeriz.	1.4	2.1	1.8	3.2	3.6
Envrionmen.	3.1	2.6	4.0	3.2	3.6
Total	8.6	9.0	10.7	10.3	11.5

2.2 Problems & Prospects of Industrial Pollution in recent times:

Indian chemical industries have grown at exponential rate for the last 30 years. Their contribution to the exports as well as import substitution by indigenous production in the over all national economy and industrial growth is substantial. In the industries we put some input like raw material, energy sources, water, air, manpower etc. We also receive output in form of product, contaminated effluents, gases, sludge etc. We send effluent to the river or sea or lakes after treatment of it whereas gases are emitted in the environment. We must have to follow the norms which are given by the state and central government. However compliance of norms is not good enough for sustainable and healthy environment and ecology. Though there is a perceptible improvement in the environment scenario in the last one or two decades, there still exists a wide gap between mere compliance of statutory environmental norms and in-built, intrinsic, self-sustaining, spontaneous, genuine, willful and sustainable, comprehensive environmental measures by the industry. Unless this gap is filled by appropriate, industry-friendly measures, mechanisms and interventions, there is a great danger that environment and ecology and eventually energy and economy would be annihilated over a period of coming decades.

2.3 Limitations of the Conventional Treatments:

It is well known that impurities present in the wastewater like complex organic compounds, refractory and hazardous compounds in a dissolved state can not be removed easily by conventional treatments. These compounds are so strongly bonded by the covalent bonds that it is difficult to “rupture” the bonds by the chemical as well as biological methods so as to convert them into carbon dioxide, water etc. These compounds are highly toxic. Beside, action of the enzymatic degradation by the microbes on some of the organic compounds in the effluent is so slow due to their “Robust” configuration that it takes several months to obtain the desired level of purification. Such prolonged hydraulic retention time in the traditional biological treatments make the capital cost of the treatments prohibitively high thanks to their correspondingly large volumes. [5]

2.4 Different Advance Oxidation methods:

Advance Oxidation is the generic term covering several chemical oxidative treatments, which are capable of "rupturing" the stable, robust configuration of the complex compounds by virtue of their strongly penetrative oxidative power. Such oxidation of the organics compounds into breakdown of a complex molecule into less harmful or innocuous compounds thereby resulting in reduction COD, color, BOD, and toxicity.

Various basic chemical processes and techniques are summarized as advance oxidation methods below:

1. **Ozone as an oxidant:** Ozone is a very strong oxidant, more powerful that other oxidants commonly used in water and wastewater treatment. The use of ozonation as a treatment process began with the application of ozone as a disinfectant of drinking water. Ozone decomposes rapidly in water to form more reactive secondary oxidants, the most important being the hydroxyl radical. The formation of the hydroxyl radical is important in that OH radical is a more powerful and less selective oxidant than ozone. As a result many compounds that are unreactive with ozone can be oxidized by OH. [12]

[A] Ozone-hydrogen peroxide (peroxone):

Mechanism: Although H2O2 reacts very slowly with the ozone molecule in water, its conjugate base (HO_2^-) can rapidly react with molecular ozone, thereby the formation of hydroxyl radicals in two steps:

$$H_2O_2 + H_2O \longrightarrow HO_2^- + H_3O^+ \qquad (1)$$

$$HO_2^- + O_3 \longrightarrow {}^{\cdot}OH + O_2^- + O_2 \qquad (2)$$

At every low concentration, the HO_2^- ion will be very effective in initiating ozone decomposition and facilitating the formation of hydroxyl radicals. The HO_2^- ions consumed by ozone are then regenerated by shifting the chemical equilibrium to the left according to first reaction. The higher the pH, the more H_2O_2 that will be dissociated into HO_2^- ions. As a result the ozone decomposition rate will increase with increasing pH. After hydroxyl radicals are formed, the propagation of radical chain reactions and the oxidation of contaminants follow the same mechanisms as those occurring in ozonation at elevated pH.

Applications: In water treatment, the O_3 - H_2O_2 process has been mainly used for the oxidation of micro pollutants, the removal of pesticides, and the control of taste and odour-causing materials. It was also tested for contaminated groundwater and wastewater treatment. The removal of color from the three effluent streams from a pulp and paper mill, O_3 - H_2O_2 process could achieve color removal up to 85% for the caustic extract stream, up to 90% for the acidic stream, and up to 50% in the final effluent.

[B] Ozone-Ultraviolet radiation:

Reaction mechanism: The O_3-UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals. Because he maximum absorption of ozone molecules is at 253.7 nm, the light source commonly used is a medium-pressure mercury lamp wrapped in a quarts sleeve. It can generate the UV light at a wavelength of 200-280 nm.

The reaction mechanism starts with activating the ozone molecule by UV to form oxygen radicals, which then combine with water to form $\cdot OH$ radicals:

$$O_3 + h\nu \longrightarrow O_2 + O(^1D) \qquad (3)$$

$$O(^1D) + H_2O \longrightarrow 2\ \cdot OH \qquad (4)$$

The UV photolysis of ozone would also yield H_2O_2:

$$O(^1D) + H_2O \longrightarrow H_2O_2 \qquad (5)$$

The formed H_2O_2 can be further photolyzed to form two $\cdot OH$ radicals. Alternatively, it could be first dissociated into HO_2^- and then participate in a series of chain reactions along with ozone to produce hydroxyl radicals as occurs in the O_3 - H_2O_2 process. As the photolysis of H_2O_2 molecules is very slow, the second pathway is most likely to be predominant at neutral pH range for ozone decomposition. Thus O_3-UV process resembles the O_3 - H_2O_2 process in terms of reaction mechanism and the increased rate of organic destruction can be explained by H_2O_2 catalyzed decomposition of ozone. It should be noted that other reaction mechanisms could also contribute to the increased rate of organic compound oxidation by the O_3-UV process. UV radiation can lead to the direct excitation of some organic compounds. The excited compounds then react with ozone molecules to form various degradable products. Thus the efficiency of this mechanism would be enhanced by the high concentration of ozone. In normal case, ozone itself will absorb UV light, competing with organic compounds for UV energy.

Applications: The O_3-UV process was initially developed for the destruction of wastewaters containing cyanide. Since then, it has been tested to oxidize aliphatic and aromatic chlorinated or organic contaminants and pesticides. Its use for the treatment of clear groundwater containing trichloroethylene and perchloroethylene had been commercialized by the early 1980s. However, the O_3-UV process is now considered less economical compared with the O3 - H_2O_2 and H_2O_2 –UV processes in most cases.

[C] Hydrogen peroxide-Ultraviolet:

Mechanism: Under UV radiation, H_2O_2 will be photolyzed to form two hydroxyl radicals. The formed hydroxyl radicals then react with organic contaminants or undergo an H_2O_2 decomposition-formation cycle:

$$H_2O_2 + h\nu \longrightarrow 2\ {}^{\cdot}OH \qquad (6)$$

$$H_2O_2 + {}^{\cdot}OH \longrightarrow H_2O + HO_2 \qquad (7)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (8)$$

The formation-decomposition cycle of H2O2 was used to explain a nearly constant concentration of H_2O_2 during treatment. It is interesting to note that the H_2O_2 will also act as a scavenger for hydroxyl radicals as shown earlier, in which case an excessive H_2O_2 dose might hinder the radical degradation. On the other hand sufficient H_2O_2 is necessary so that it can absorb UV to accelerate the generation of hydroxyl radicals. Unlike ozone, H_2O_2 has an exceptionally low molar absorptivity within the wavelength range of 200-300 nm. Thus it is particularly susceptible to the competing absorption of UV by organic compounds and suspended solids in water.

Applications: Like the O_3-UV process, the H_2O_2-UV process is mainly used for the oxidation of refractory contaminants. For example, oxidation of atrazine with H_2O_2-UV. Result showed that, depending upon the initial atrazine concentration, more than 99% of the atrazine can degraded in less than 15 min.

[D] Fenton's Reagent:

Hydrogen peroxide is a powerful oxidant with a radoxpotenital of +1.77V for the two electron reduction to water. Nevertheless due to the slow rate at which most organic are oxidized by hydrogen peroxide in the treatment of organic hazardous waste should be used in combination with Fe or low wavelength UV irradiation.

Fenton's reagent is powerful oxidant. In the presence of Fe^{+2} , hydrogen peroxide decomposes to form the hydroxyl radical, $^{\cdot}OH$.

$$Fe^{+2} + H_2O_2 \longrightarrow OH^- + {}^{\cdot}OH + Fe^{+3} \qquad (9)$$

The $^{\cdot}OH$ radical can react with an organic compound C, or it can be scanvenged by Fe^{+2} or hydrogen peroxide.

$$C + {}^{\cdot}OH \longrightarrow \text{products} \qquad (10)$$

$$Fe^{+2} + {}^{\cdot}OH \longrightarrow OH^- + Fe^{+3} \qquad (11)$$

$$H_2O_2 + {}^{\cdot}OH \longrightarrow H_2O + HO_2 \qquad (12)$$

It has been proposed the regeneration of Fe^{+2} occur via a series of steps

$$Fe^{+3} + H_2O_2 \longrightarrow [FeOOH_2^+] + [H^+] \qquad (13)$$

$$FeOOH_2^+ \longrightarrow HO_2^- + Fe^{+2} \qquad (14)$$

$$Fe^{+3} + HO_2^- \longrightarrow Fe^{+2} + [H^+] \qquad (15)$$

The addition of Fe^{+2} will tend to be more effective in promoting the degradation of organic compounds than the addition of Fe^{+3} . However, the presence of Fe^{+3} may enhance the production of OH radicals, particularly if Fe^{+2} is also present.

Fenton's reagent is known to oxidize organic compounds. The reaction rate has been shown to increase with increase in pH. However, at pH greater than 4 to 5, ferric ion precipitates and consequently the reaction slows down. The decrease in the reaction rate is presumed to be due in part; to the fact that iron atoms buried in the precipitate are not accessible to the hydrogen peroxide.

[E] Ozone–hydrogen peroxide–UV radiation (O3/H2O2/UV):

The addition of H2O2 to the O3/UV process accelerates the decomposition of ozone, which results in an increased rate of OH generation. In processes involving pollutants that are weak absorbers of UV radiation, it is more cost effective to add hydrogen peroxide externally at a reduced UV flux. If direct photolysis of pollutants is not a major factor, O3/H2O2 should be considered as an alternative to photo oxidation processes.

The capital and operating costs for the UV/O3 and/or H2O2 systems vary widely depending on the wastewater flow rate, types and concentrations of contaminants present, and the degree of removal required. Table presents a comparison of the operating costs of various AOPs.

Table – 2.4.E.1 Comparative operating costs of some AOPs

Process	Cost of oxidant	Cost of UV
O3/UV	High	Medium
O3/H2O2	High	0
H2O2/UV	Medium	High
Photo catalytic oxidation	Very low	Medium to high

Applications:

The UV/oxidation technology (O3/H2O2/UV system) has been applied success-fully for the removal of volatile organic contaminants (VOC) (benzene, acetone, dichloroethane, tetrachloroethane, etc.) from groundwater in San Jose, CA (USA) . Greater than 90% removal efficiencies were achieved for most VOC. During1994, a UV/oxidation system was installed at the Milan Army Ammunition Plant(Milan, TN, USA) to treat holding ponds contaminated with explosive compounds(2,4,6-trinitrotoluene, 2,4- and 2,6-dinitrotoluenes, nitrobenzene, etc.) . GAC filtration follows the UV/ozone oxidation step. In 1994, UV/O3/H2O2 treatment was installed at the Bofors Nobel Superfund Site, located near Muskegon, MI (USA), for the decomposition of hazardous wastewaters containing benzene, toluene, chlorobenzene, tetrachloroethane, benzidine, etc.

[F] High temperature oxidative reactions:

High temperature thermal treatment is generally given to highly concentrated secondary sludge, which, due to its high organic content, is not easily biodegradable.

Thermal reduction of sludge involves the total or partial conversion of organic solids to oxidized end products, primarily carbon dioxide and water, by incineration or wet air oxidation.

The partial oxidation and volatilization of organic solids by pyrolysis or starved air combustion to end products and energy.

The major advantages of these processes are:

- Volume reduction to the optimum
- Destruction of pathogens and toxic compounds
- Energy can be recovered

But the main problems regarding this methodology are its expenses of installation, possible air nuisance, disposal of residuals etc. The main thermal reduction processes include multiple hearth incineration, co-incineration, fluidized bed incineration, wet air oxidation and wet oxidation in vertical, deep-well reactors.

Another advance oxidation process known as “Photo catalytic degradation” is fully described in later sections.

2.5 What is photo catalytic degradation?

Photo catalysis is a process in which the illumination of suitable semiconductor produces photo excited electrons and holes. The electron or hole can migrate to the surface and participate in half-cell reactions that may for a catalytic cycle. Conventionally this solar energy is directly used for the degradation. But presently reactions and processes are carried out with electric arc lamps, fluorescent lamps or lasers. Table 2.5 shows the oxidation potentials of commonly used oxidants. The higher the oxidation potential, the greater the decomposing capability of the material.

Table 2.5 Oxidation potentials of various oxidants [32]

Oxidants	Oxidation potential (V)
OH radicals	2.80
O 3 (ozone)	2.07
H2O2 (hydrogen peroxide)	1.77
ClO2 (hypochlorous acid)	1.49
Cl (chlorine)	1.36

2.6 Principle of Photo degradation. [3]

A brief outline of some basic concepts of photo degradation is presented here. In order for photo chemistry to take place, photons of light must be absorbed. The energy of a photon is given by

$$U = hc/\lambda \qquad (16)$$

Where h is a plank’s constant ($6.626 * 10^{-34}$ J s), c is a speed of light and λ is the wavelength. For a molecule’s bond to be broken, U must be greater than the energy of that bond.

When a given wavelength λ of light enters a medium, its special irradiance E_{λ} (Wm^{-2} nm^{-1}) is attenuated according to the Lambert-Beer law which is expressed in two ways, one for gas phase and other for liquid phase:

$$\ln (E^{o}{}_{\lambda} / E^{l}\lambda) = \alpha_{\lambda} p_i l \qquad \text{gas phase} \qquad (17)$$

$$\log (E^{o}{}_{\lambda} / E^{l}{}_{\lambda}) = \epsilon_{\lambda} c_i l \qquad \text{liquid phase} \qquad (18)$$

$E^{o}{}_{\lambda}$ and $E^{l}{}_{\lambda}$ are the incident spectral irradiances and at a distance l into the medium, α_{λ} is the absorption coefficient (cm^{-1} atm^{-1}) , pi is the partial pressure of component i, ϵ_{λ} is the extinction coefficient (M^{-1} cm^{-1}) and ci is the concentration of component i. The absorbance A λ at wavelength λ is the product of $\epsilon_{\lambda} c_i l$. The photochemical quantum yield is defined as number of molecules of target compound that reacts divided by number of photons of light absorbed by the compound, as determined in a fixed period of time.

The term photo catalysis implies the combination of photochemistry with catalysis. Both light and catalyst are necessary to achieve or to accelerate a chemical reaction. Photo catalysis may be defined as the “acceleration of a photoreaction by the presence of catalyst.” Heterogeneous processes employ semiconductor slurries for catalysis, whereas homogeneous photochemistry is used in single phase system. In heterogeneous photo catalysis, dispersed solid particles absorb larger fractions of the UV spectrum efficiently and generate chemical oxidants in situ from dissolved oxygen or water. [5]

2.7 About Titanium Dioxide catalyst [13]

Background

Titanium has been used commercially for just over 50 years and in this short time it has achieved a reputation equal to an invincible comic book hero. In its pure form titanium is strong as steel, but 45% lighter, and compared to aluminum it is 60% heavier and twice as strong. Titanium is lightweight, with good strength, and excellent corrosion resistance, but is alloyed with other metals to increase its strength.

Melting Point of titanium is 1668 degrees C and burns in the presence of air or nitrogen. Titanium has the distinction of being the only element that burns in a nitrogen atmosphere

Light waves interacting with the surface oxide of titanium (TiO2) produce beautiful and the vivid colors on the surface of titanium. When pure, titanium dioxide is relatively clear and has an extremely high index of refraction with an optical dispersion higher than diamond. [13]

Titanium (Ti) ore was first discovered in 1791, and named after the Titans, mythological first sons of the earth. **Pure metallic titanium was not produced until 1910**. Some 40 years later a global titanium industry began to form. **The worlds 4th most abundant structural metal**, exceeded only by aluminum, iron, and magnesium.

Titanium is the 9th most abundant element, constituting about 0.63% of the Earths crust. Found in, Australia, United States, Canada, South Africa, Sierra Leone, Ukraine, Russia, Norway, and Malaysia.

World Demand

Some 94 percent of World demand for titanium is in the form of Titanium Dioxide (Ti02), and about 6 percent in titanium metal and metal alloys. The principal end uses for Ti02 are pigments. Other uses include catalysts, ceramics, coated fabrics and textiles, floor coverings, printing ink, and roofing granules.

Corrosion Resistant

Titanium is immune to corrosion from salt-water, most industrial and organic chemicals. This is due to titanium's very thin, tenacious and highly protective surface oxide Ti02. If worn or scratched, the oxide layer will immediately restore itself in the presence of air or water. Titanium dioxide is one of the most basic materials in of daily life; used widely paints, cosmetics and food stuffs.

Titanium dioxide, also known as titania is the naturally occurring oxide of titanium, chemical formula **TiO2**.

Titania exists in a number of crystalline forms the most important of which are anatase and rutile. Pure titanium dioxide does not occur in nature but is derived from ilmenite or leuxocene ores. It is also readily mined in one of the purest forms, rutile beach sand. These ores are the principal raw materials used in the manufacture of titanium dioxide pigment. The first step is to purify the ore, and is basically a refinement step. Either the sulphate process, which uses sulphuric acid as an extraction agent or the chloride process, which uses chlorine, may achieve this. After purification the powders may be treated (coated) to enhance their performance as pigments.

Brief description of Titanium Dioxide: [31]

Strongest, most brilliant white available to artists in the entire history of art. Its chemical stability is likewise outstanding.

Figure – 2.7.1 Sources of Titanium Dioxide Whites:

Anatase Rutile

Generally titanium dioxide is of two type: 1) anatase 2) rutile

In the above figure the mineral sources of titanium dioxide is shown. Titanium dioxide can be the mixture of both anatase as well as rutile or it can be in separate or powder form also. In this dissertation powder form of titanium dioxide has been used.

About the chemical structure: [29]

Chemical name: Titanium Dioxide

Formula: TiO_2

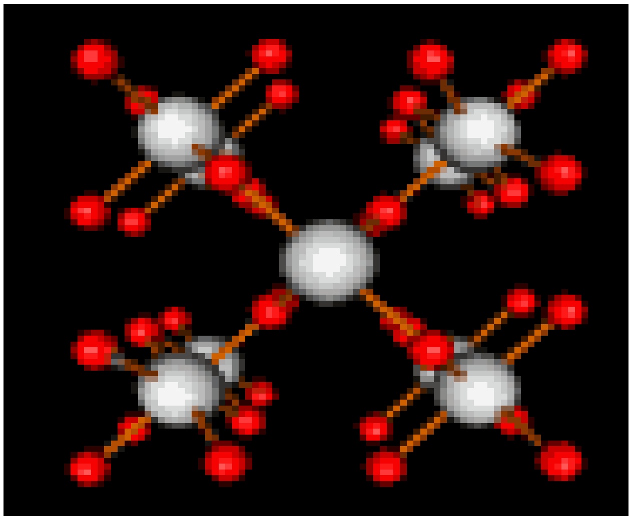


Figure – 2.7.2 3D- model of TiO_2 (grey-Ti, red-O_2)

Figure 2.7.3 Crystal structure of anatase:

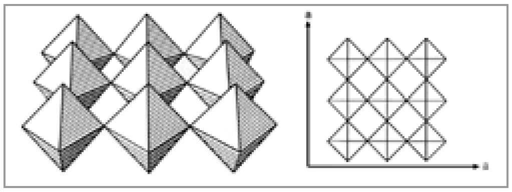
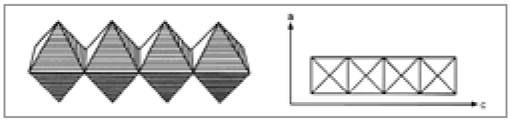


Figure 2.7.4 Crystal Structure of Rutile:



Key Properties: [14]

Physical and mechanical properties of sintered titania are summarized in table 1, while optical properties of titania are provided in table 2.

Table 2.7.1. Typical physical and mechanical properties of Titania. [14,27]

Property	Value
Density	4 gcm^{-3}
Porosity	0%
Modulus of Rupture	140MPa
Compressive Strength	680MPa
Poisson’s Ratio	0.27
Fracture Toughness	3.2 $Mpa.m^{-1/2}$
Shear Modulus	90GPa
Modulus of Elasticity	230GPa
Microhardness (HV0.5)	880
Resistivity (25°C)	10^{12} ohm.cm
Resistivity (700°C)	$2.5x10^{4}$ ohm.cm
Dielectric Constant (1MHz)	85
Dissipation factor (1MHz)	$5x10^{-4}$
Dielectric strength	4 $kVmm^{-1}$
Thermal expansion (RT-1000°C)	9 x 10^{-6}
Thermal Conductivity (25°C)	11.7 WmK^{-1}
Melting point	1850 °C
Boiling point	2500 °C
Flash point	Non-flammable
Solubility	insoluble

Table- 2.7.2. Optical properties of Titania. [14]

Phase	Refractive Index	Density ($g.cm^{-3}$)	Crystal Structure
Anatase	2.49	3.84	Tetragonal
Rutile	2.903	4.26	Tetragonal

Table – 2.7.3 Thermodynamic properties of TiO2 [26]

$\Delta_f H^\ominus$gas	−249 kJ/mol
$\Delta_f H^\ominus$ liquid	−879 kJ/mol
$\Delta_f H^\ominus$ solid	−944 kJ/mol
$S^\ominus$ solid	51 J/mol·K

Chemical reactions of the elements [28]

Reaction of titanium with air:

Titanium metal is coated with an oxide layer that usually renders it inactive. However once titanium starts to burn in air it burns with a spectacular white flame to form titanium dioxide, TiO_2 and titanium nitride, TiN. Titanium metal even burns in pure nitrogen to form titanium nitride.

$$Ti(s) + O_2(g) \rightarrow TiO_2(s)$$

$$2Ti(s) + N_2(g) \rightarrow TiN(s)$$

Reaction of titanium with water

Titanium metal is coated with an oxide layer that usually renders it inactive. However, titanium will react with steam form the dioxide, titanium (IV) oxide, TiO_2, and hydrogen, H_2.

$$Ti(s) + 2H_2O(g) \rightarrow TiO_2(s) + 2H_2(g)$$

Reaction of titanium with the halogens

Titanium does react with the halogens upon warming to form titanium (IV) halides. The reaction with fluorine requires heating to 200°C. So, titanium reacts with fluorine, F_2, chlorine, Cl_2, bromine, I_2, and iodine, I_2, to form respectively titanium(IV) bromide, TiF, titanium(IV) chloride, TiCl, titanium(IV) bromide, TiBr, and titanium(IV) iodide, TiI.

$$Ti(s) + 2F_2(g) \rightarrow TiF_4(s) \text{ [white]}$$

$$Ti(s) + 2Cl_2(g) \rightarrow TiCl_4(l) \text{ [colorless]}$$

$$Ti(s) + 2Br_2(g) \rightarrow TiBr_4(s) \text{ [orange]}$$

$$Ti(s) + 2I_2(g) \rightarrow TiI_4(s) \text{ [dark brown]}$$

Reaction of titanium with acids

Dilute aqueous hydrofluoric acid, HF, reacts with titanium to form the complex anion $[TiF_6]^{3-}$ together with hydrogen, H_2.

$$2Ti(s) + 12HF(aq) \rightarrow 2[TiF_6]^{3-}(aq) + 3H_2(g) + 6H^+(aq)$$

Titanium metal does not react with mineral acids at ambient temperature but does react with hot hydrochloric acid to form titanium (III) complexes.

Reaction of titanium with bases

Titanium does not appear to react with alkalis under normal conditions, even when hot.

Whenever different semiconductor materials have been tested under comparable conditions for the degradation of the same compounds, TiO2 has generally been demonstrated to be the most active. Only ZnO is as active as TiO2. **TiO2's strong resistance to chemical and photo corrosion, its safety and low cost limits the choice of convenient alternatives.** This semiconductor is of special interest, since it can use natural (solar) UV because it has an appropriate energetic separation between its valence and conduction bands which can be surpassed by the energy content of a solar photon ($\lambda > 300$ nm). Other semiconductor particles, e.g., CdS or GaP absorb larger fractions of the solar spectrum and can form chemically activated surface-bond intermediates, but unfortunately, these photo catalysts are degraded during the repeated catalytic cycles involved in heterogeneous photo catalysis. Therefore, degradation of the organic pollutants present in wastewater using irradiated TiO2 suspensions is the most promising process and R&D in this field has grown very quickly during the last years.

Applications [15]

Applications for sintered titania are limited by its relatively poor mechanical properties. It does however find a number of electrical uses in sensors and electro catalysis. By far its most widely used application is as a pigment, where it is used in powder form, exploiting its optical properties.

Pigments

The most important function of titanium dioxide however is in powder form as a pigment for providing whiteness and opacity to such products such as paints and coatings (including glazes and enamels), plastics, paper, inks, fibers and food and cosmetics.

Titanium dioxide is by far the most widely used white pigment. Titania is very white and has a very high refractive index – surpassed only by diamond. The refractive index determines the opacity that the material confers to the matrix in which the pigment is housed. Hence, with its high refractive index, relatively low levels of titania pigment are required to achieve a white opaque coating.

The high refractive index and bright white color of titanium dioxide make it an effective opacifier for pigments. The material is used as an opacifier in glass and porcelain enamels, cosmetics, sunscreens, paper, and paints. One of the major advantages of the material for exposed applications is its resistance to discoloration under UV light.

Photo catalysis

Many studies have been published on the use of **TiO2** as a photo catalyst for the decomposition of organic compounds. **TiO2** is active under UV light

Photo catalytic activity (PCA) is the ability of a material to create an electron hole pair as a result of exposure to ultraviolet radiation. The resulting free-radicals are very efficient oxidizers of organic matter. Photo catalytic activity in **TiO2** has been extensively studied because of its potential use in sterilization, sanitation, and remediation applications. The ability to control PCA is important in many other applications utilizing **TiO2** including paint pigments and cosmetics that require low PCA. [10]

Oxygen Sensors

Even in mildly reducing atmospheres titania tends to lose oxygen and become sub stoichiometric. In this form the material becomes a semiconductor and the electrical resistivity of the material can be correlated to the oxygen content of the atmosphere to which it is exposed. Hence titania can be used to sense the amount of oxygen (or reducing species) present in an atmosphere.

Antimicrobial Coatings

The photo catalytic activity of titania results in thin coatings of the material exhibiting self cleaning and disinfecting properties under exposure to UV radiation. These properties make the material a candidate for applications such as medical devices, food preparation surfaces, air conditioning filters, and sanitary ware surfaces.

Other Areas of activity in titanium dioxide photo catalysis.
1 fog proof, and self cleaning glass
2 anti-bacterial, anti-viral, fungicidal
3 anti-soiling, self cleaning
4 deodorizing, air purification
5 water treatments, water purification

Where do reserves of TiO2 exist:
1. Southeast Canada
2. Southeast USA
3. Southwest Scandinavia
5. Midwest and South Africa
6. Mediterranean Sea
7. East Australia

2.8 Chemistry of Photo catalytic degradation

If the nucleus of an atom were the sun in our solar system, the electrons revolving around the nucleus would be the orbiting planets. The path that an electron travels is referred to as an "orbit." There is a limit to the number of electrons that can occupy one orbit. Electrons in the outermost orbit are referred to as "valence electrons." Valence electrons are responsible for the bonding of atoms.

As a result of solid-quantum effects, semiconductor materials posses two allowable electron energy bands. The lower energy region is the valence band; electrons in this energy band are binding electrons and are somewhat restricted in movement. The higher region is the conduction band. These electrons, to a first approximation, are free to move throughout the solid and produce conductivity similar to that of metals. Between these two regions is a forbidden zone, or band gap. Where there is no electron energy, is referred to as a "forbidden band."

Photo excitation in a semiconductor occurs as the absorption of radiation of energy equal to, or greater than, the band gap energy excites and electron into the conduction band of the solid. There is, correspondingly, an electro vacancy or hole that remains in the valence band.

$$\text{Semiconductor} \xrightarrow{h\nu} e^- + h^+$$

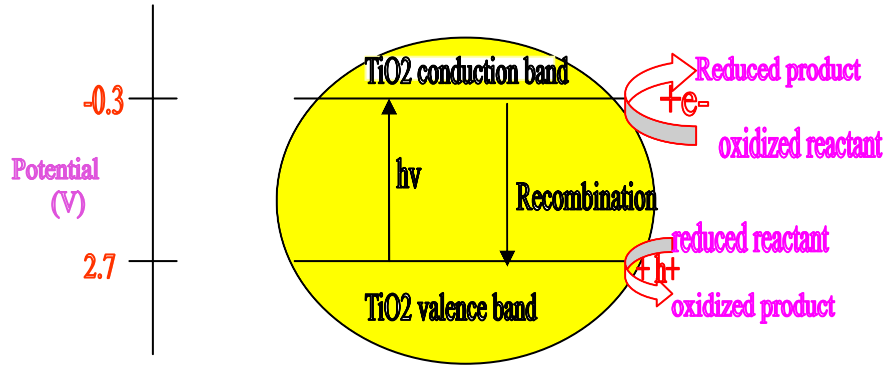


Figure 2.8

Creation of electron-hole pairs in
illuminated semiconductors, and subsequent photocatalytic redox reactions

These holes, having affinity for electrons, are very strong oxidizing agents. The number of electron-hole pairs is dependent on the intensity of the incident light and the material's electronic characteristics that prevent them from recombining and releasing the absorbed energy. Similarly, the hole can migrate by a valence band electron filling the vacancy, leaving behind another hole in the previous position. The band gap energy and corresponding wavelength required for excitation for some common semiconductors are given in the table.

Table – 2.8 some common semiconductors, their band gap energy and corresponding excitation wavelength

Semiconductor	Band gap (eV)	Wavelength (nm)
TiO_2	3.0-3.2	413-388
ZnO	3.2	388
ZnS	3.7	335
CdS	2.4	516
Fe_2O_3	2.3	539
WO_3	2.8	443

The semiconductor potentials for the valence band and conduction band are significantly different. This difference avoids rapid recombination of the e^- - h^+ pairs. The band potentials are a function of pH and decrease by 0.059 V per pH unit increase as predicted by the Nernst equation.

The holes in the semiconductor solid are attracted to the oxide/sulfide surface, where they oxidize an adsorbed water molecule or hydroxide ion.

$$h^+ + H_2O\ (ads) \longrightarrow {}^{\cdot}OH + H^+$$

$$h^+ + OH^- \longrightarrow {}^{\cdot}OH$$

Hydroxyl radicals are very reactive neutral species with an unpaired electron. They react rapidly and nonselectively in the oxidation of organic compounds and are the common oxidizers.

2.8.1 Titanium Dioxide surface reactions:

Titanium dioxide is rapidly hydrated in aqueous solution due to the partially uncoordinated states of its surface titanium and oxygen atoms. The amphoteric nature of the hydrated TiO2 surface results in pH-dependent equilibrium between protonated and deprotonated hydrous surface species.

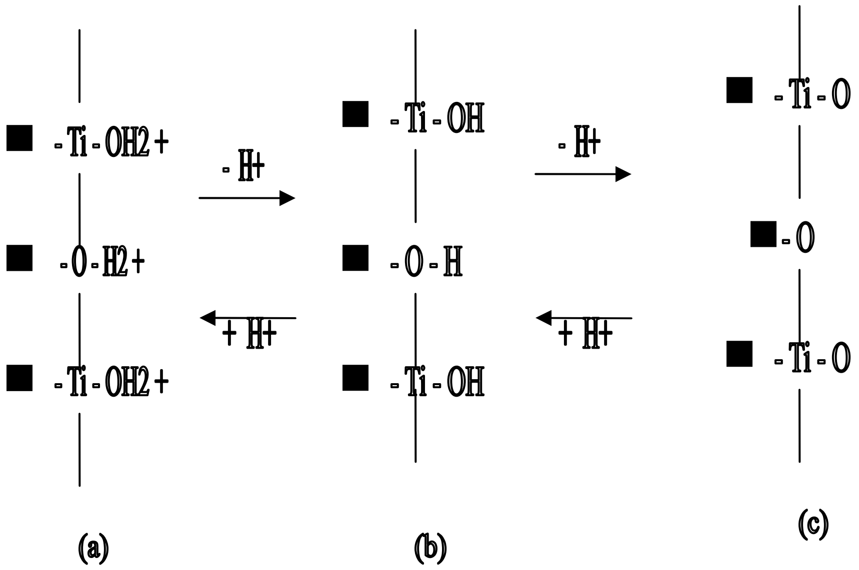


Figure 2.8.1 Titanium Dioxide surface reactions

Where ■ represents the bulk solid. The pH at which the overall TiO_2 surface is neutrally charged is termed the zero point of charge or pH $_{zpc}$. Reported values for TiO_2 range from 3.5 to 6.7 depending on purity and crystal structure. TiO_2 can be viewed as a solid diprotic acid having two acidity constants. The theoretical maximum surface coverage of TiO_2 with surface hydroxo groups is 5-15 OH groups per square nanometer.

Thermodynamically permissible traps for valence band holes in aqueous TiO_2 systems include adsorbed water molecules or hydroxide ions, which react with the holes to produce hydroxyl radicals. Hydroxyl radicals have been detected by electron spin resonance (ESR) in illuminated aqueous TiO_2 suspensions and are widely believed to be the most important oxidizing species in these systems. Oxidizable species such as hydrocarbons (RH) or other organic contaminants in the solution subsequently react with the hydroxyl radicals.

$$RH + {}^{\cdot}OH \longrightarrow ROH$$

Continued radical attack will result in the complete oxidation of the organic compound via pathways common to all hydroxyl radical oxidations.

Adsorbed organic species may react with valence band holes at the TiO_2 surface, resulting in the formation of an organic radical. Despite the favorable thermodynamics of such a reaction, however, there is strong evidence that H_2O and $OH^{\cdot}$ and not organic compounds, are the principal hole traps in TiO_2 photo catalytic systems.

In most cases, that oxidation can be continued so that the final products are CO2, H2O, and inorganic ions of other elements present in the organic molecule (this outcome is termed mineralization). The problems which have limited the widespread commercialization of this attractive technology to date are the material handling problems presented by the fine particulate nature of TiO2 and the fact that the TiO2 polar surface is not favorable for adsorption of organics in competition with water.

To date, evidence supports the idea that the hydroxyl radical (•OH) is the main oxidizing specimen responsible for photo oxidation of the majority of the organic compounds studied. The first effect, after absorption of near ultraviolet radiation, $\lambda < 390$ nm, is the generation of electron/hole pairs (see Figure), which are separated between the conduction and valence bands. In order to avoid recombination of the pairs generated, if the solvent is oxidoreductively active (water) it also acts as a donor and acceptor of electrons. Thus, on a hydrated and hydroxylated TiO2 surface, the holes trap •OH radicals linked to the surface. In any case, it should be emphasized that even trapped electrons and holes can rapidly recombine on the surface of a particle. This can be partially avoided through the capture of the electron by preadsorbed molecular oxygen, forming a super oxide radical. [15, 18, 19]

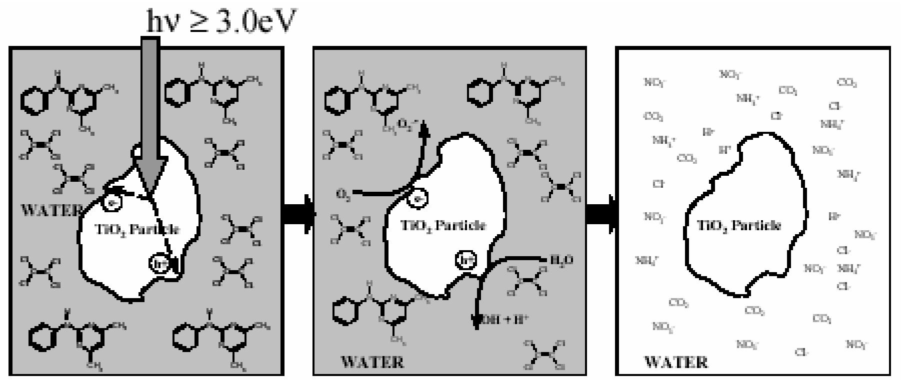


Figure: 2.8.2 Effect of UV radiation on a TiO2 particle dispersed in water and subsequent destruction of the organics dissolved in water.

CHAPTER 3

EXPERIMENTAL SETUP

3.1 Project Experimental set-up:

In ATIRA, I have to conduct experiments for getting better reduction in COD by this method. For that I require TiO_2 catalyst and ultra violet lamp which are provided by the ATIRA. I have been using TiO2 catalyst in powder form. As I have shown the properties of TiO_2 catalyst in the literature review, I have not discussed those things again.

01-02-06 11:01 am

Figure- 3.1 TiO_2 powder

Titanium dioxide that I am going to use for this project as shown above figure, I have given it for further analysis purpose at CSMCRI (Central Salt and Marine Chemicals Research Instiute) Bhavnagar. I got results as below:

Area:

Particle name: Titanium dioxide   size range: 0.02 to 20000 µm
Surface weighted mean D[3,2]: 3.519 µm   specific surface area: 1.70505 m^2/gm
Single Point Surface Area at P/Po 0.20057321: 10.3596 m^2/g
BET Surface Area: 10.6310 m^2/g

Langmuir Surface Area: 14.6248 m^2/g

Micropore Area: 1.3536 m^2/g

External Surface Area: 9.2774 m^2/g

BJH Adsorption Cumulative Surface Area of pores
between 17.000000 and 3000.000000 A Diameter: 9.3969 m^2/g

BJH Desorption Cumulative Surface Area of pores
between 17.000000 and 3000.000000 A Diameter: 10.5651 m^2/g

Volume:

Single Point Adsorption Total Pore Volume of pores less than
725.0691 A Diameter at P/Po 0.97256591: 0.020724 cm^3/g

Micro pore Volume: 0.000549 cm^3/g

BJH Adsorption Cumulative Pore Volume of pores
between 17.000000 and 3000.000000 A Diameter: 0.043707 cm^3/g

BJH Desorption Cumulative Pore Volume of pores
between 17.000000 and 3000.000000 A Diameter: 0.044477 cm^3/g

Pore Size:

Adsorption Average Pore Diameter (4V/A by BET): 77.9770 A

BJH Adsorption Average Pore Diameter (4V/A): 186.0485 A

BJH Desorption Average Pore Diameter (4V/A): 168.3933 A

I have shown the main summary of my particle size and pore size distribution analysis. The full report I have given in appendix-c in my report.

After that my ultra violet lamp comes in picture. There are several types of ultra violet lamps available in the market. I have shown the specifications of ultra violet lamp that I am going to use for my experiments

UV-light specifications:
Total watt - 20 watt
Wavelength - 254 nm
Flow rate - 200 LPH
Material of construction – SS 304

Figure – 3.1.1 Ultra Violet Lamps in running condition

As shown in the figure, the UV-light is in working condition. It is placed inside the stainless steel casing shown in below figure. SS casing has Outer diameter is 60 mm and length is 290 mm. UV-lamp has length of 265 mm.

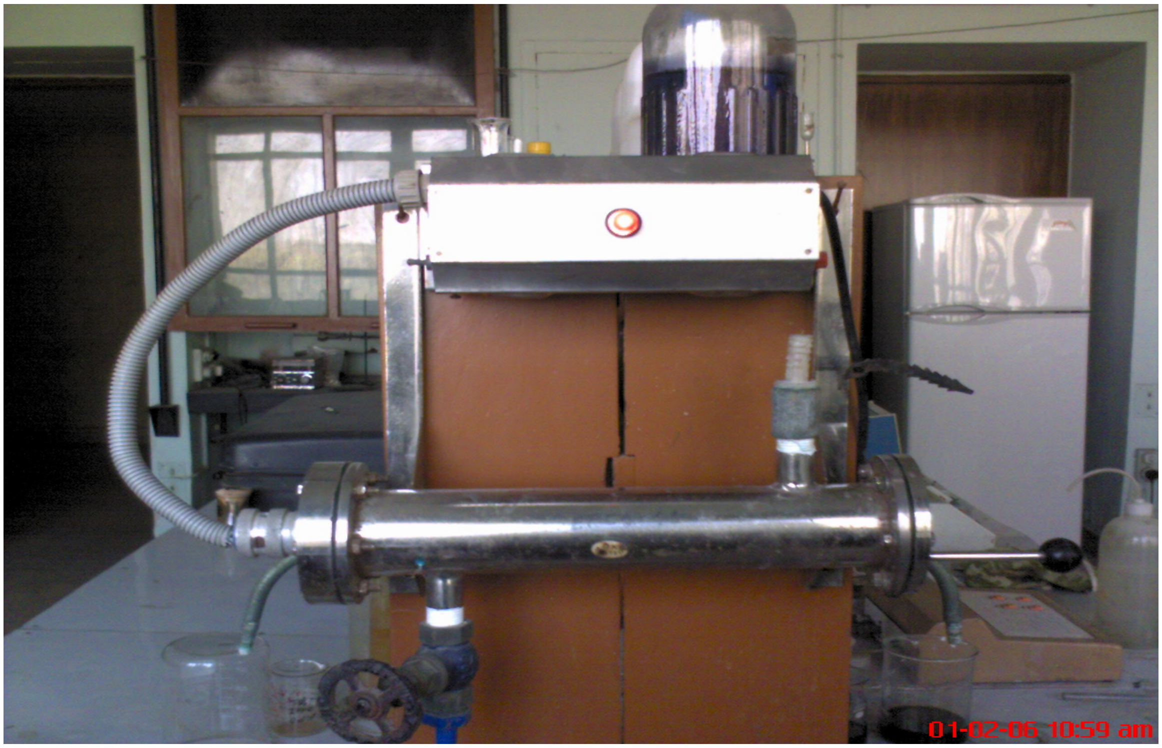


Figure- 3.1.2 Ultra violet lamp fitted in steel casing

Ultraviolet (UV) light is electromagnetic energy with wavelengths ranging from 100 to 400 nm. This energy spectrum lies between X-rays and visible light. The UV energy spectrum can be divided into four ranges:

- Vacuum UV (100 – 200 nm)
- UV-C (200 – 280 nm)
- UV-B (280 – 315 nm)
- UV-A (315 – 400 nm)

UV light, in relatively low doses, is effective on bacteria, viruses, and protozoa. UV light between 200 nm and 300 nm has a germicidal effect. The optimum germicidal UV range is between 250 and 270 nm.

The major benefits of UV disinfection are that it is environmentally safe, producing no harmful disinfection by-products, and by virtue of replacing chlorine as a disinfectant, eliminates chlorine toxicity in the mixing zone. Although, recent research indicates that in water treatment plants there is a potential for a photo reactivation of organisms, as DNA damage is repaired with exposure to sunlight following UV irradiation; this is not considered a significant concern for sewage treatment plants. This phenomenon has been shown to decrease with higher initial UV dosage.

Ultraviolet light is produced in wastewater disinfection systems by mercury vapor lamps. Three main types of lamps are available that are characterized by both their operating pressure and their output level: low pressure/low intensity lamps (LP/LI), low pressure/high intensity lamps (LP/HI), and medium pressure/high intensity lamps (MP/HI). Conventional low pressure, low intensity UV lamps produce essentially monochromatic radiation at 253.7 nm. The advantage of high intensity lamps is increased UV output resulting in a lower number of bulbs being required. Medium pressure lamps produce a wider wavelength than low intensity lamps; however, there is no more output from the medium pressure bulb in the 254 nm range, the most effective disinfection wavelength. The primary benefit of medium pressure systems are the greatly reduced number of lamps that are required. As a broad guideline, or rule of thumb, these systems are not practical for use at wastewater treatment plants having average flow rates less than 30 MLD - 40 MLD because equipment components are more expensive, power 1consumption is higher, and bulb life is shorter. Also, they operate at very high temperatures, requiring special cooling features, and require self-cleaning lamps to ensure the quartz sleeves do not foul. UV treatment applications are well suited to, but need not be confined to tertiary effluent only.

Recent advances in options offered by manufacturers of UV treatment systems include variable output electronic ballasts to match power output to effluent flow, and well as self cleaning lamps. Electronic ballasts, as opposed to electromagnetic ballasts, are now standard. Also, most low pressure UV lamps are non-proprietary, and have an effective useful life of more than 10,000 hours in operation, and the cost of medium pressure lamps are now similar to the cost of low pressure lamps.

CHAPTER 4

RESULTS AND DISCUSSION

Now initially for starting of the experiments, I have decided to go with synthetic effluent. So I prepared synthetic dye & had kept it for 10, 20, 30 minutes without passing through UV light. Then measured certain parameters like pH, COD, color etc. before and after treatment. Then again took 150 ml of synthetic solution and kept it through UV light without adding TiO2 catalyst for 10, 20, 30 minutes.

In both the cases I have got the following results.

Table 4.1

Parameters	Initial	Final
pH	3.9	3.9
COD	976 mg/l	975.6
Color	-	-

So from the above results, we can conclude that for the COD reduction we must have to use catalyst as well as UV –light.

After these experiments, took the same synthetic effluent for the photo catalytic treatment. Initially I wanted to test the solution contain around 1000 mg /lit of COD. So prepared it as shown below with the results.

Synthetic effluent:
1000 ml water + 1 gm blue dye

Table – 4.2 % COD reduction for the synthetic effluent

Time (min)	pH	Initial COD	Final COD	% reduction
0	3.9	976	-	-
10	6.44	976	896	8.1
20	6.36	976	884	9.42
30	6.23	976	852	12.7
40	6.74	976	624	36.06

50	6.58	976	518.78	46.84
60	6.58	976	494.54	49.32
70	6.6	976	389	**60.14**
80	6.36	976	364.55	62.64
90	6.9	976	349.66	64.17
100	6.77	976	340.54	**65.10**
110	6.4	976	340.54	65.10
120	6.38	976	351	64.03
130	6.36	976	350.45	64.09
140	6.4	976	356.14	63.51

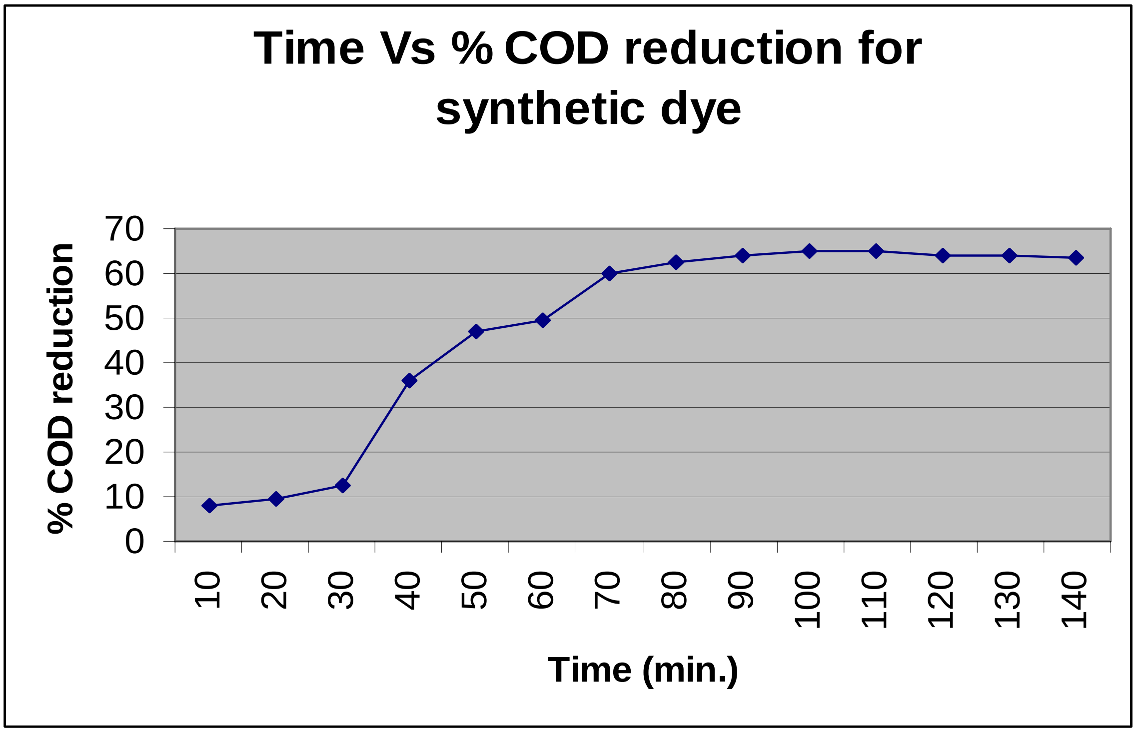


Figure – 4.1 Time Vs % COD reduction for synthetic dye

In this case I could achieve around 65% of COD reduction at 100 min. after that my COD remains either constant or decreasing with respect to time as shown in the graph. This 65% reduction is maximum in this case but if you see the table then at 70 min. reduction is around 60%. And after more 30 min. overall reduction is 65%. So within 30 min. % reduction increases only up to 5%. Now second graph shows the reduction of initial COD.

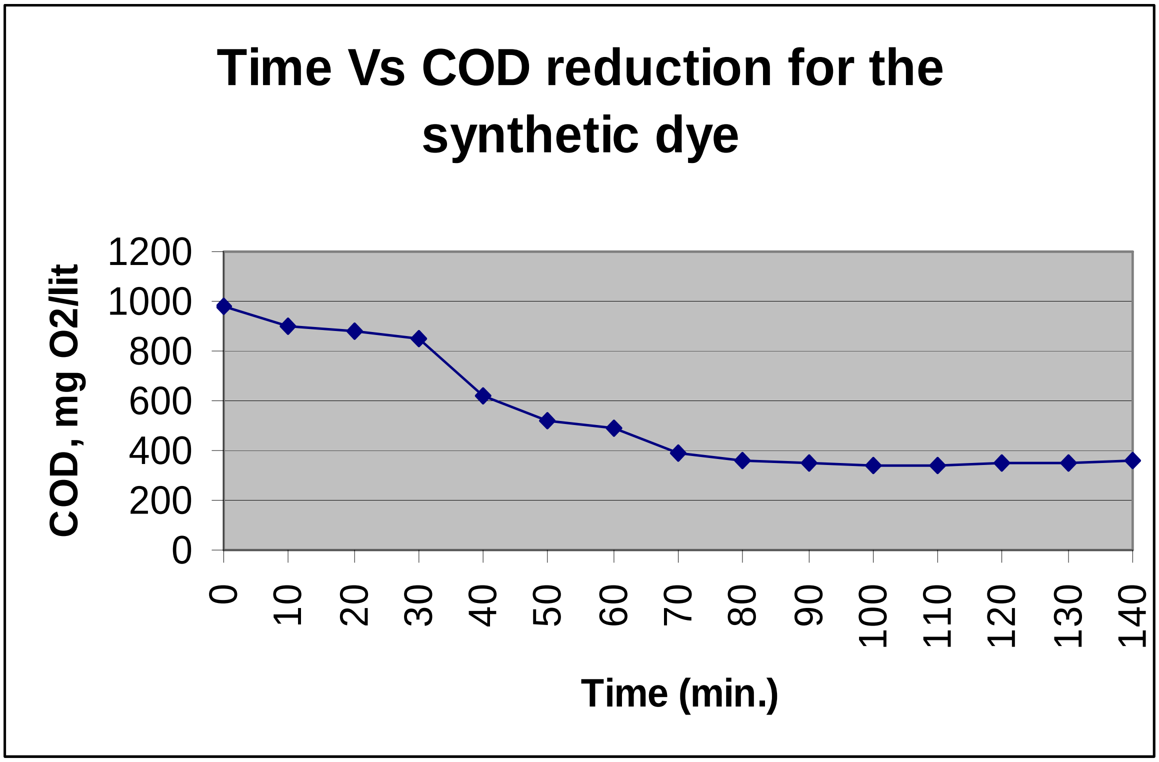


Figure- 4.2 Time Vs COD reduction for synthetic dye

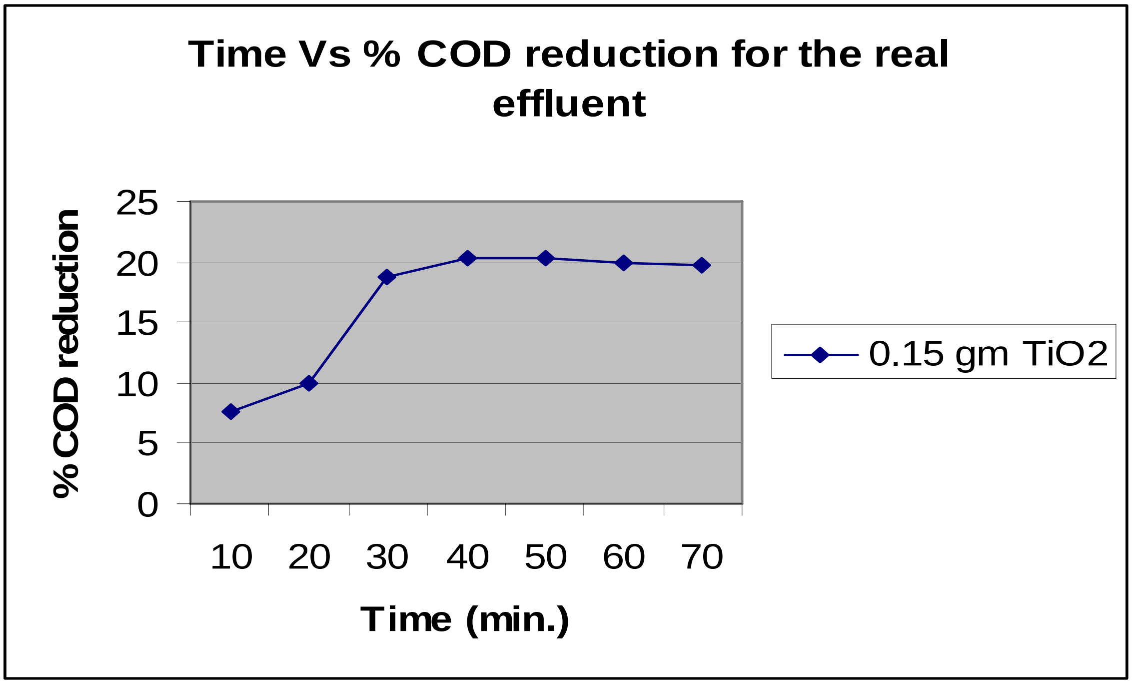
After doing the experiments for the synthetic effluent, I did for the real effluent. But this time took various concentration of my catalyst. I wanted to see the effect of TiO2 catalyst at different concentration with respect to time.

This time I have chosen the effluent of **Common Effluent Treatment Plant.**

Table 4.3 % COD reduction of CETP effluent

Time (min)	pH	Initial COD	Final COD	% reduction
0	7.14	1584	-	-
10	7.68	1584	1464	7.57
20	7.64	1584	1410	10

30	7.64	1584	1287	18.75
40	7.77	1584	1263	20.26
50	7.76	1584	1262	**20.32**
60	7.69	1584	1269	19.88
70	7.66	1584	1270.23	19.8



<u>Figure – 4.3 Time Vs % COD reduction for the real effluent</u>

After plotting the graph for the 0.15 gm of TiO2, I took 0.1 gm & 0.05 gm of TiO2 for the optimum concentration of TiO2 with respect to maximum reduction of COD.

<u>0.1 gm TiO2:</u> **<u>Table 4.4</u>**

Time (min.)	COD , mg /lit	% reduction
0	1600	-
10	1325	17.14
<u>20</u>	1268	**<u>20.71</u>**
30	1268	20.71
40	1270.4	20.6
50	1270.94	20.56

<u>0.05 gm TiO2:</u> **<u>Table 4.5</u>**

Time (min.)	COD, mg /lit	% reduction
0	1600	-
10	1350	15.62
20	1300	18.75
30	1299	**18.8**
40	1302.12	18.61
50	1302.46	18.59

Now for these concentration ranges, I plotted the graph as shown below.

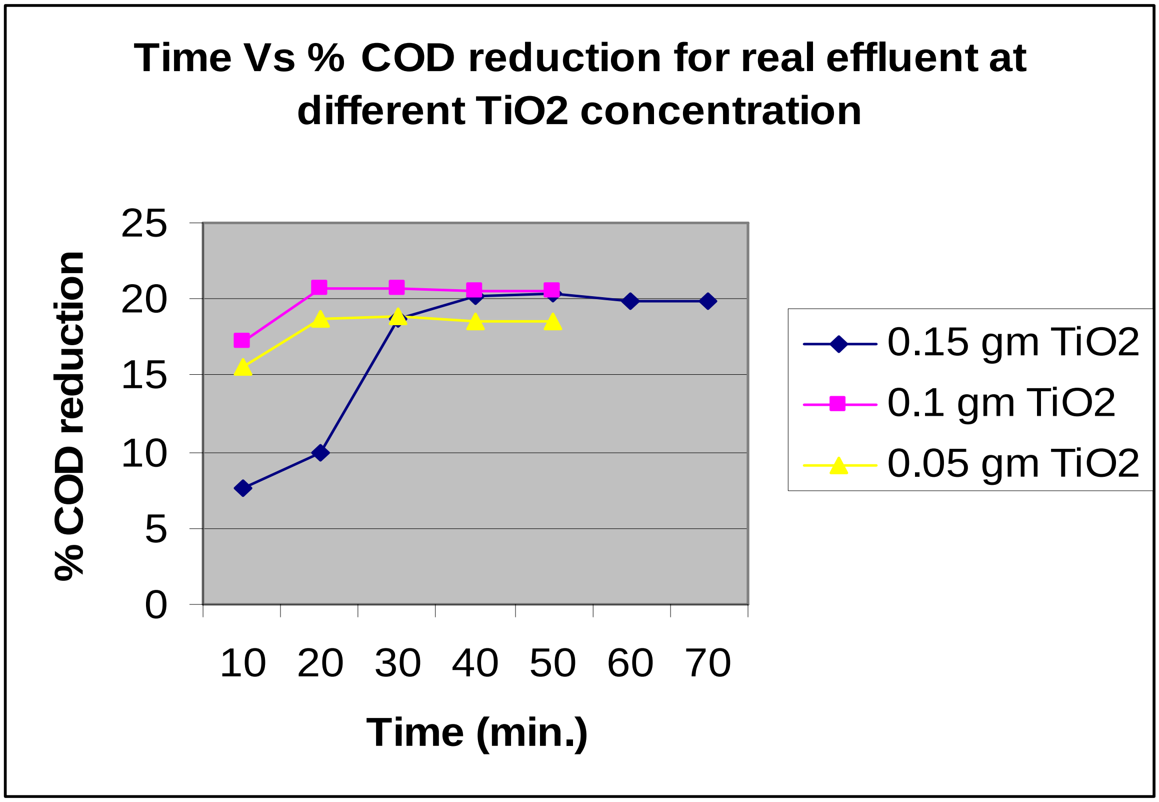


Figure 4.4 Time Vs % COD reduction for real effluent at different TiO2 concentrations

So far I achieved around 20% reduction of COD with adding TiO2 at different concentration. In this real effluent case, we could achieve around 20% reduction within 20min. of 0.1gm TiO2. Now from the literature I came across the Fenton's reagent which acts as a strong oxidizing agent and gives better reduction in COD.

So initially took synthetic effluent for checking the effect of Fenton's reagent combining with TiO2 at different concentration with respect to time.

Synthetic effluent: TiO2 + FeS + H2O2

Time: 10 min., 1.5ml (FeS + H2O2 each)

Table 4.6

TiO2 (gm)	Initial COD (mg/lit)	Final COD (mg/lit)	% reduction
0.15	934	200	78.5
0.1	934	150	83.9
0.05	934	140	**85**

I got the 85% reduction of COD within 10 min. Where as in case of without Fenton's reagent I could achieve around 65% reductions in COD within 100 min.

Now once again I started experiments for the real **Synthetic and Polymer industry's effluent** at different TiO2 concentration range.

Time: 10 min. (with Fenton's reagent)

Table 4.7

TiO2 (gm)	Initial COD (mg/lit)	Final COD (mg/lit)	% reduction
0.15	7300	5120	**29.86**
0.1	7300	5080	**35.41**
0.05	7300	5100	**30.13**

Time: 20 min. (with Fenton's reagent)

Table 4.8

TiO2 (gm)	Initial COD (mg/lit)	Final COD (mg/lot)	% reduction
0.15	10933.3	8106.6	25.85
0.1	10933.3	8906.6	18.53
0.05	10933.3	9120	16.58

Time: 30 min. (with Fenton's reagent)

Table 4.9

TiO2 (gm)	Initial COD	Final COD	**%** reduction
0.15	7360	7253	18.5
0.1	7360	5920	19.56
0.05	7360	5706.6	22.46

Now I have plotted the graph of % COD reduction with Fenton's reagent as shown below.

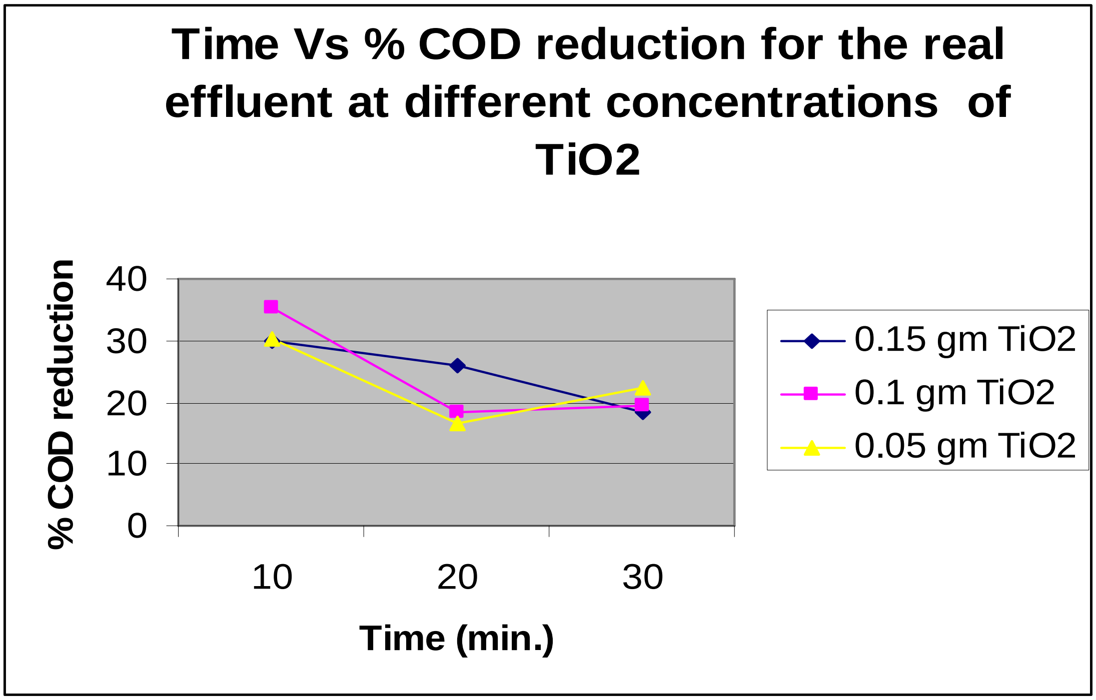


Figure 4.5 Time Vs % COD reduction for the real effluent at different concentrations of TiO2 with Fenton's reagent

Without adding FeS & H2O2:

Time: 10 min.

Table 4.10

TiO2 (gm)	Initial COD	Final COD	% reduction
0.15	7300	5024	**29.2**
0.1	7300	5280	**27.67**
0.05	7300	5248	**28.10**

Time : 20 min.

Table 4.11

TiO2	Initial COD	Final COD	% reduction
0.15	10933.3	8320	23.9
0.1	10933.3	9546.66	12.68
0.05	10933.3	8853.3	19.02

Time: 30 min. **Table 4.12**

TiO2 (gm)	Initial COD	Final COD	% reduction
0.15	7360	6933.3	5.79
0.1	7360	6293.3	14.49
0.05	7360	6986	5.07

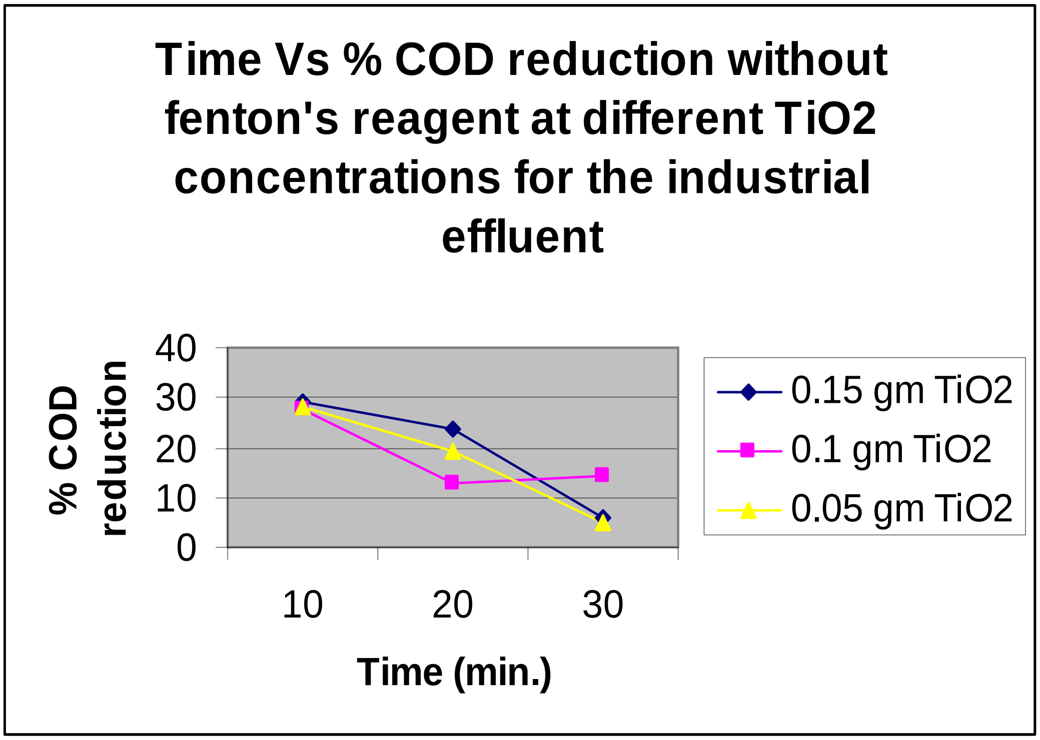


Figure 4.6 Time Vs % COD reduction without Fenton's reagent at different TiO2 concentration for the real effluent

We can see from the tables that without adding Fenton' s reagent I could achieve around 29% reduction within 10 min. where as by adding it 35% reduction within 10 min. I expected more than 50% reduction in case of Fenton's reagent but I could not achieve that level in this effluent.

Now I took another industrial effluent which contained more than 30000 mg/lit of COD. By doing these experiments, I wanted to see the effect of photo catalytic degradation for very much higher initial COD of effluent.

Caffeine: TiO2 + (FeS + H2O2)

Time: 10 min: 1.5 ml (FeS + H2O2)

Table 4.13

TiO2 (gm)	Initial COD	Final COD	% reduction
0.15	33120	29200	11.83
0.1	33120	31466.66	5
0.05	33120	31733.33	4.18

Time: 20 min.

Table 4.14

TiO2 (gm)	Initial COD	Final COD	% reduction
0.15	38400	33600	12.5
0.1	38400	33507.84	12.74
0.05	38400	32800	14.58

Time: 30 min

Table 4.15

TiO2 (gm)	Initial COD	Final COD	% reduction
0.15	36400	24122	**33.73**
0.1	36400	28000	23.07
0.05	36400	30800	15.38

Time: 40 min.

Table 4.16

TiO2 (gm)	Initial COD (mg/lit)	Final COD (mg/lit)	% reduction
0.15	36400	27756	23.74
0.1	36400	28832	20.79
0.05	36400	30810	15.35

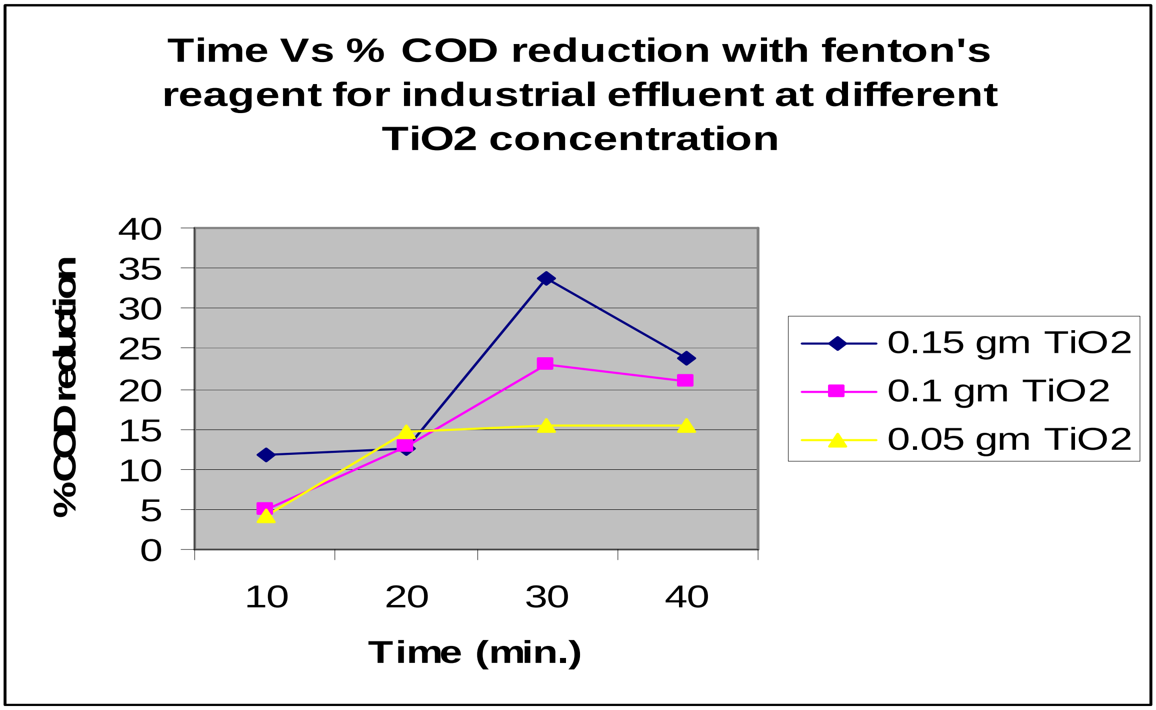


Figure 4.7 Time Vs % COD reduction with Fenton's reagent for industrial effluent at different TiO2 concentrations

Without (FeS & H2O2):

Time: 10 min **Table 4.17**

TiO2 (gm)	Initial COD	Final COD	% reduction
0.15	33120	31400	0.05
0.1	33120	30200	8.81
0.05	33120	31400	0.05

Time: 20 min. **Table 4.18**

TiO2 (gm)	Initial COD	Final COD	% reduction
0.15	38400	36400	5.2
0.1	38400	34800	9.3
0.05	38400	37200	3.12

Time: 30 min. **Table 4.19**

TiO2 (gm)	Initial COD	Final COD	% reduction
0.15	36400	27600	**24.17**
0.1	36400	29600	18.68
0.05	36400	29600	18.68

Time : 40 min: **Table 4.20**

TiO2 (gm)	Initial COD (mg/lit)	Final COD (mg/lit)	% reduction
0.15	36400	27853	23.48
0.1	36400	29712	18.37
0.05	36400	29753	18.26

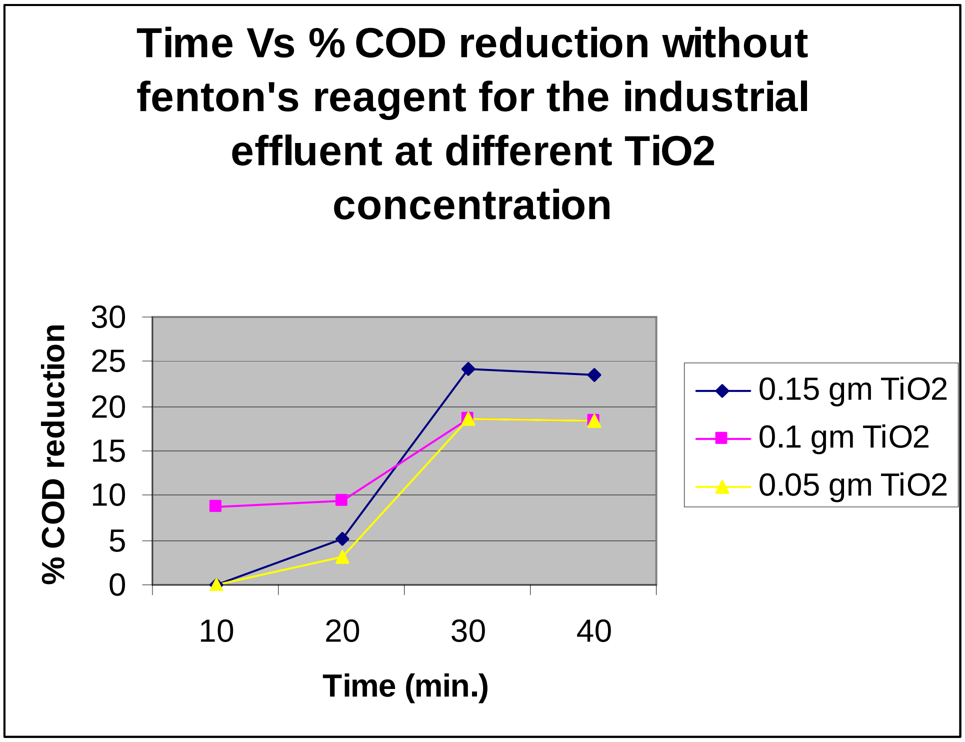


Figure 4.8 Time Vs % COD reduction without Fenton's reagent for industrial effluent at different TiO2 concentration

In this case for the same time and same concentration of TiO2 with adding Fenton's reagent degradation is higher than without Fenton's reagent.

CHAPTER 5

CONCLUSION AND FURTHER WORK SCOPE

The main aim of this project is to reduce the level of COD by using photo catalytic method for the real effluent. At industrial scale if we go for reduction of individual compound, operating cost as well as capital cost would be increase. The combination of advance oxidation techniques, which is found very useful at industrial level. It could be concluded from the results mentioned in previous chapter, that the synergistic combination of advance oxidation technologies, particularly Fenton's reaction with photo catalysis give more degradation in COD for the real as well as synthetic effluent. Normally in this case cost of UV-lamp is Rs.183.33, 366.66,550 for 10, 20 & 30 min. respectively.

Here titanium dioxide is in very fine powder form so after the treatment we could recover it around 98.5 to 99%. As it is insoluble we should get 100% recovery but due to its powder form it is very difficult. But at the other side we have advantage of its low commercial prize. At commercial level TiO2 cost is Rs.142/Kg. Where as at laboratory scale cost is Rs.230 per 500 gm. So it is cheap at commercial scale.

Moreover it has been observed that some manufacturing units were not complying with norms specified by the regulatory agencies due to their conventional treatment system. They are expecting the closure notice from the government. In such units advance oxidation process can be useful. But for that more research is to be carried out for reduction in COD as low as possible. So it has been observed that advance oxidation process has tremendous scope in future in the field of effluent treatment problems and their remedies.

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APPENDICES

APPENDIX: A

CHEMICAL OXYGEN DEMAND (COD)

A.1 General

Chemical Oxygen Demand (COD) test determines the oxygen required for chemical oxidation of most organic matter and oxidizable inorganic substances with the help of strong chemical oxidant. The test can be employed for the same purpose as the BOD test taking into accounts its limitations. The intrinsic limitation of the test lies in its inability to differentiate between the biologically oxidizable and biologically inert material.

COD determination has an advantage over BOD determination in that the result can be obtained in about 3 hours, as compared to 5 days required for BOD test. Further the test is relatively easy, gives reproducible results and is not affected by interference's as the BOD test.

A.2 Application of COD data

1. Extensively used in the analysis of domestic and industrial wastewater.
2. In conjunction with BOD test, COD test is helpful in indicating toxic conditions and the presence of biologically resistant organic substances.
3. COD test is used widely in the operation of treatment facilities because of the speed with which results can be obtained.

A.3 Principle

Reflux digestion method

The organic matter and oxidizable inorganic substances present in water or wastewater get oxidized completely by standard potassium dichromate ($K_2Cr_2O_7$) in the presence of H_2SO_4 to produce $CO_2 + H_2O$. The excess $K_2Cr_2O_7$ remaining after the reaction is titrated with ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2$]. The dichromate consumed gives the O2 required for the oxidation of organic matter. The contents are refluxed for 2 hours.

Reactions are as under:

$$\mathbf{2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2}$$

$$\mathbf{C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O}$$

In order for K2Cr2O7 to oxidize organic matter, the solution is made acidic. An excess of K2Cr2O7 must be present in COD analysis. Hence excess is added and actual amount reduced is determined. Ferrous ammonium sulfate is used for back titration.

The test is based on the principle that all organic compounds can be oxidized by strong oxidizing agents in acidic media. Hence:

- COD values are always greater than BOD values. COD values are too large, if greater amounts of biologically resistant organic matter is present, i.e. lignin.
- COD value do not provide any information on the rate at which actual biodegradation will take place.
- Reflux condensers are used to prevent loss of volatile organic compounds.

A.4 Interferences

1. Fe (II) and hydrogen sulfide exert COD of 0.14 mg/mg Fe^{2+} and 0.47mg/mg H_2S respectively.
2. The chlorides interference is eliminated by addition of mercury salt (mercury sulfate), which precipitates chlorides as $HgCl_2$: $Hg^{2+} + 2\ Cl^- = HgCl_2$. Although 1 g $HgSO_4$ is specified for 50 mL sample, a lesser amount may be used where sample chloride concentration is known to be less than 2000 mg/L or as long as a 10:1 ratio of $HgSO_4$:Cl^- is maintained.
3. Addition of Ag2SO4 to concentrated H2SO4 acts as a catalyst to stimulate the oxidation of straight chain aliphatic and aromatic compounds.
4. Nitrite (NO^{2-}) exerts a COD of 1.1 mg/mg NO_2-N. Sulphamic acid is added at 10 mg sulfamic acid for every 1 mg of NO_2-N in the refluxing flask. Add sulfamic acid to the standard $K_2Cr_2O_7$, since it must be included in the distilled water blank.

A.5 Sample handling

Natural, not very heavily polluted water should be analyzed on the same day or at least within 24 hours. If there is to be a delay before analysis, the sample may be preserved by adding, sulfuric acid, about 2 mL H_2SO_4 (d = 1.84) to each 100 mL of sample. If samples are to be stored for longer than 24 hours, deep freezing is recommended.

Safety precautions:

1. Handling concentrated sulfuric acid, especially at the start of refluxing step requires extreme care.
2. Silver sulfate is poisonous, and hence contact with the chemical and its solution must be avoided.
3. Mercuric sulfate is very toxic and hence contact with the chemical and its solution must be avoided.

A.6 Apparatus

1. COD Reflux apparatus consisting of a flat bottom 500-mL capacity flask with condenser.
2. A heating mantle.

A.7 Chemicals Required

1. Potassium dichromate ($K_2Cr_2O_7$)
2. Sulphuric acid (H_2SO_4) - Silver sulphate (Ag_2SO_4) solution
3. Mercuric sulphate ($HgSO_4$)
4. Ferrous ammonium sulfate (FAS) [$Fe(NH_4)_2(SO_4)_2$]
5. Ferroin indicator

A.8 Reagents

1. *Standard potassium dichromate, 0.25 N*: Dissolve 12.259g of potassium dichromate (dried at 103°C for 24 h) in distilled water and dilute to 1 L.

2. *Sulphuric acid-silver sulfate reagent*: Add 10 g of silver sulfate to 1000 mL of concentrated sulphuric acid (H_2SO_4) and keep overnight for dissolution.

3. *Ferroin Indicator*: Dissolve 1.485g of 1,10-phenanthroline monohydrate and 0.695g of ferrous ammonium sulphate heptahydrate in distilled water and dilute to approximately 100ml.

4. *Standard ferrous ammonium sulfate (FAS), 0.25 N*: Dissolve 98 g of ferrous ammonium sulphate hexahydrate in about 400 mL distilled water. Add 20ml of concentrated sulphuric acid (H_2SO_4). Cool and dilute to exactly 1L. The ferrous ammonium sulfate (FAS) titrant must be standardized daily by the following procedure:

Dilute 10ml of standard potassium dichromate ($K_2Cr_2O_7$) solution to 100ml with distilled water. Slowly add 30ml of concentrated sulphuric acid and cool to room temperature. Titrate with ferrous ammonium sulphate titrant, using 2 to 3 drops (0.10 to 0.15 ml) of Ferroin indicator.

Normality of FAS = [(ml $K_2Cr_2O_7$) * 0.25] / (ml of FAS required)

The deterioration of FAS can be decreased if it is stored in a dark bottle.

A.9 Procedure

1. Take a 500 mL capacity flat-bottom conical flask and add 0.4 g of $HgSO_4$.
2. Add 20 mL of sample or an aliquot of sample diluted to 20 mL with distilled water and mix well.
3. Add few glass beads followed by 10 mL of potassium dichromate depending upon the expected COD.
4. Add slowly 30 mL concentrated sulfuric acid + silver sulfate reagent and mix thoroughly. The slow addition along with swirling prevents fatty acids to escape out due to high temperature.

5. Mix well. If the color turns green, take either fresh sample with lesser eliquot or add more dichromate and sulfuric acid. Connect the flask to condenser. Mix the contents before heating. Improper mixing will result in bumping and sample may be blown out.
6. Reflux for a minimum of 2 hours. Cool and then wash down the condenser with distilled water.
7. Dilute for a minimum of 150 mL (about 300 mL), cool to room temperature and titrate excess potassium dichromate remaining after refluxing with corresponding standard ferrous ammonium sulfate using ferroin as an indicator (8-10 drops). Sharp color change from blue green to wine red indicates end point or completion of the titration.
8. Perform blank in the same manner using distilled water instead of sample.

A.10 Calculation

COD (mg/l) = [(A - B) * (N) * 8 * 1000] / sample size (ml)

where:
A= mL of [$Fe(NH_4)_2(SO_4)_2$] used for blank
B = mL of [$Fe(NH_4)_2(SO_4)_2$] used for sample
N = normality of FAS titrant [$Fe(NH_4)_2(SO_4)_2$]
8 = milliequivalent weight of oxygen.

▸ **Sample Calculation**: Table 4.1 observation 7: COD = 215 mg/L
⇨ COD (mg/l) = [(A - B) * (N) * 8 * 1000] / sample size (ml)
A = 24.5 mL, B = 20.5 mL, N = 0.1, Sample size = 15 mL
$\therefore$ COD = [(24.5 – 20.5) * 0.1 * 8000] / 15 = 215 mg/L

Source:
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APPENDIX: B

Effluent quality and discharge norms given by the Gujarat Pollution Control Board (some important parameters)

Parameters	GPCB Limits
pH	6.5-8.5
Color	100
TDS	2100 mg/l
TSS	100 mg/l
Phenolic comp.	1 mg/l
NH3-N	50 mg/l
COD	250 mg/l
BOD	30 mg/l
SS	100 mg/l
Oil & Grease	10 mg/l

APPENDIX: C

Titanium dioxide particle size, surface area and pore size distribution analysis:

Sample: TiO_2

Started: 4/28/06 10:06:20 AM	analysis adsorptive: N2
Completed: 4/28/06 1:30:30 PM	analysis bath: 77.48K
Report time: 5/1/06 PM	Thermal correction: NO
Sample weight: 0.3765 gm	smoothed pressure: NO
Warm free space: 16.99 cm^3 measured	cold free space: 50.02 cm^3
Equivalent interval: 5 sec	low pressure dose: 20 cm^3/gm STP

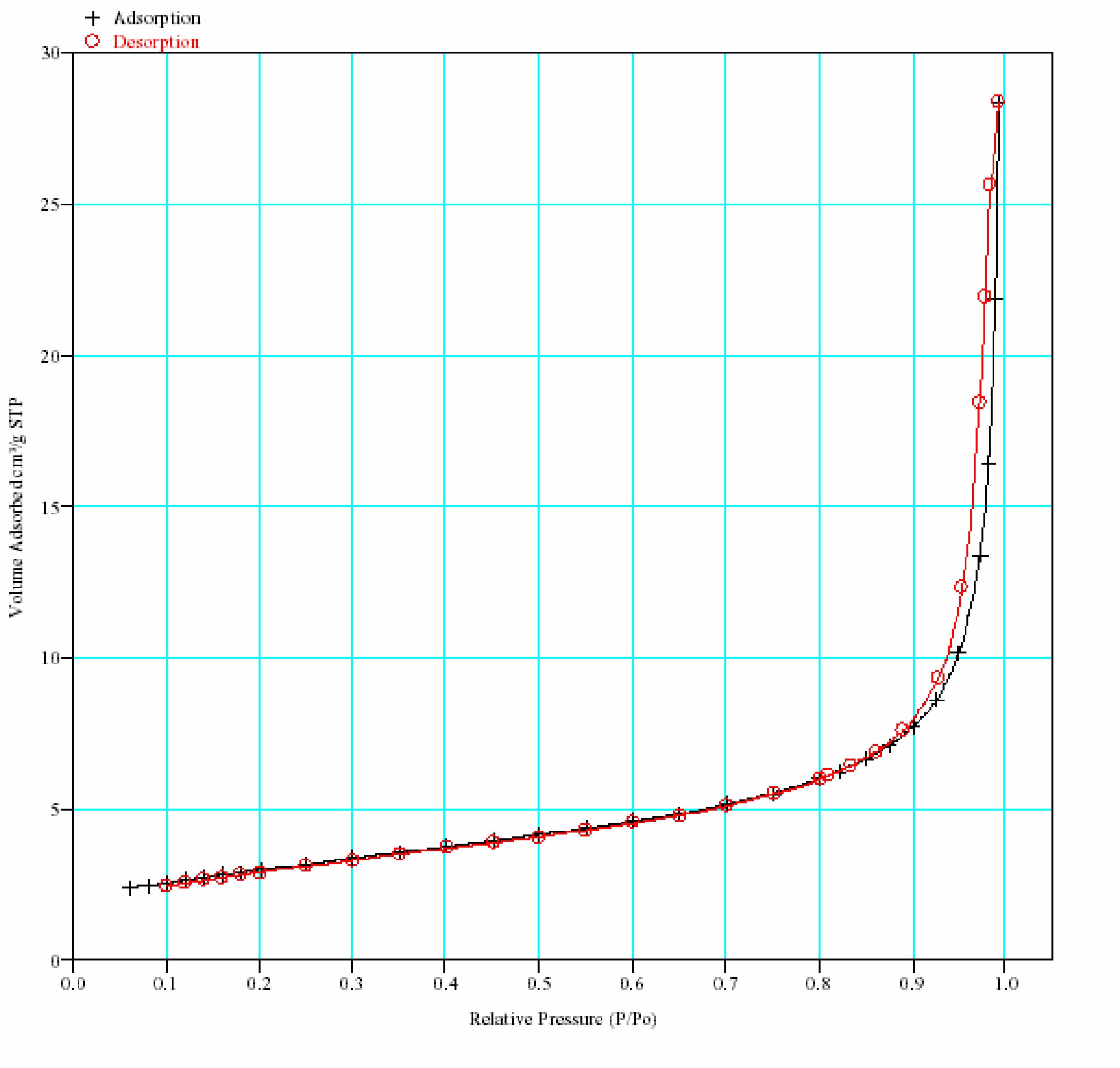
Analysis log

Relative Pressure	Pressure (mmHg)	Vol Adsorbed (cm^3/g STP)	Elapsed Time (HR:MN)	Saturation Press.(mmHg)
			00:42	772.42114
0.061847651	47.76254	2.3846	00:57	
0.080393970	62.08343	2.4728	00:59	
0.100460239	77.57726	2.5622	01:01	
0.120513078	93.05987	2.6472	01:03	
0.140512090	108.50005	2.7366	01:05	
0.160516346	123.94344	2.8195	01:07	
0.180661813	139.49307	2.8998	01:10	
0.200573214	154.86284	2.9768	01:12	
0.250496782	193.40355	3.1726	01:14	
0.300890995	232.30550	3.3750	01:16	
0.351122255	271.07574	3.5743	01:19	

0.400761137	309.38547	3.7639	01:22	
0.450579308	347.84003	3.9552	01:23	
0.500631180	386.46860	4.1576	01:25	
0.550886666	425.24634	4.3665	01:28	
0.600721984	463.70294	4.5894	01:30	
0.650755668	502.31747	4.8480	01:31	
0.700845690	540.97443	5.1555	01:32	
0.750902592	579.59674	5.5257	01:34	
0.800852976	618.13470	6.0003	01:36	
0.821130862	633.77734	6.2508	01:37	
0.851127314	656.91150	6.6748	01:39	
0.875871031	675.99036	7.1302	01:41	
0.900934905	695.31525	7.7434	01:43	
0.925658194	714.37622	8.6332	01:45	
0.949847172	733.01367	10.1717	01:48	
0.972565913	750.51501	13.3983	01:51	
0.981145425	757.07294	16.4362	01:57	
0.989045826	763.11633	21.8828	02:02	
0.993282669	766.33240	28.3941	02:07	
0.984265441	759.33350	25.6737	02:11	
0.978480514	754.82886	21.9279	02:15	
0.972336662	750.03748	18.4459	02:20	
0.953808139	735.67383	12.3330	02:27	
0.928257751	715.92719	9.3390	02:31	
0.890165255	686.51953	7.6250	02:34	
0.860982056	664.00348	6.9101	02:35	
0.835109580	644.01459	6.4479 6.4479	02:39	
0.809442108	624.20325	6.0928 6.0928	02:41	
0.802129257	618.53827	5.9834 5.9834	02:44	
			02:46	771.09912
0.751673383	579.61469	5.4999 5.4999	02:49	

0.701088392	540.60864	540.60864	5.1095	5.1095	02:51	02:51
0.650577211	501.65952	501.65952	4.7886	4.7886	02:54	02:54
0.600423843	462.98630	462.98630	4.5298	4.5298	02:56	02:56
0.550651322	424.60675	424.60675	4.2980	4.2980	02:59	02:59
0.500397311	385.85593	385.85593	4.0839	4.0839	03:01	03:01
0.450560834	347.42706	347.42706	3.8761	3.8761	03:03	03:03
0.400286559	308.66061	308.66061	3.6999	3.6999	03:06	03:06
0.350657187	270.39145	270.39145	3.5028	3.5028	03:08	03:08
0.300336885	231.58951	231.58951	3.3023	3.3023	03:10	03:10
0.250512004	193.16959	193.16959	3.1080	3.1080	03:12	03:12
0.200647586	154.71918	154.71918	2.9002	2.9002	03:15	03:15
0.180432665	139.13147	139.13147	2.8115	2.8115	03:16	03:16
0.160669572	123.89217	123.89217	2.7290	2.7290	03:18	03:18
0.140642067	108.44897	108.44897	2.6503	2.6503	03:21	03:21
0.120445530	92.87544	92.87544	2.5596	2.5596	03:22	03:22
0.100579370	77.55666	77.55666	2.4683	2.4683	03:24	03:24

Isotherm Plot



BET surface area report:

BET Surface Area: 10.6310 ± 0.0211 m^2/g

Slope: 0.406874 ± 0.000804

Y-Intercept: 0.002606 ± 0.000111

C: 157.118771

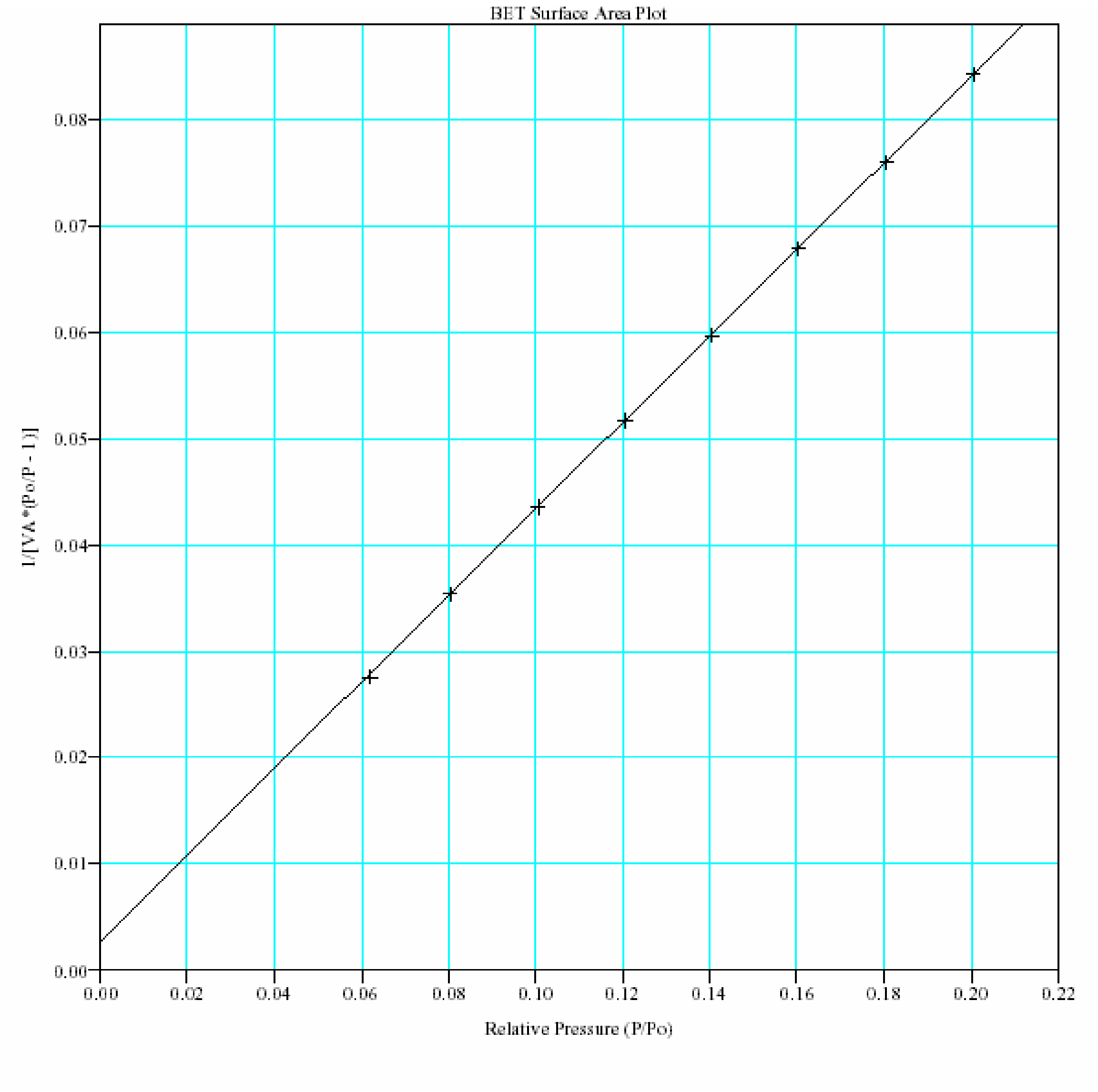
VM: 2.442123 cm^3/g STP

Correlation Coefficient: 9.999883e-01

Molecular Cross-section: 0.1620 nm^2

Relative Pressure	Vol Adsorbed (cm^3/g STP)	1/ [VA*(Po/P - 1)]
0.061847651	2.3846	0.027646
0.080393970	2.4728	0.035353
0.100460239	2.5622	0.043587
0.120513078	2.6472	0.051763
0.140512090	2.7366	0.059740
0.160516346	2.8195	0.067816
0.180661813	2.8998	0.076039
0.200573214	2.9768	0.084283

BET surface area plot:



t-plot report:

Micropore Volume: 0.000549 cm³/g

Micropore Area: 1.3536 m²/g

External Surface Area: 9.2774 m²/g

Slope: 0.599781 ± 0.003713

Y-Intercept: 0.354982 ± 0.015108

Correlation Coefficient: 9.99885e-01

Thickness Range: 3.5000 to 5.0000 A

t = [13.9900 / (0.0340 - log(P/Po))] 0.5000

Surface Area Correction Factor: 1.00

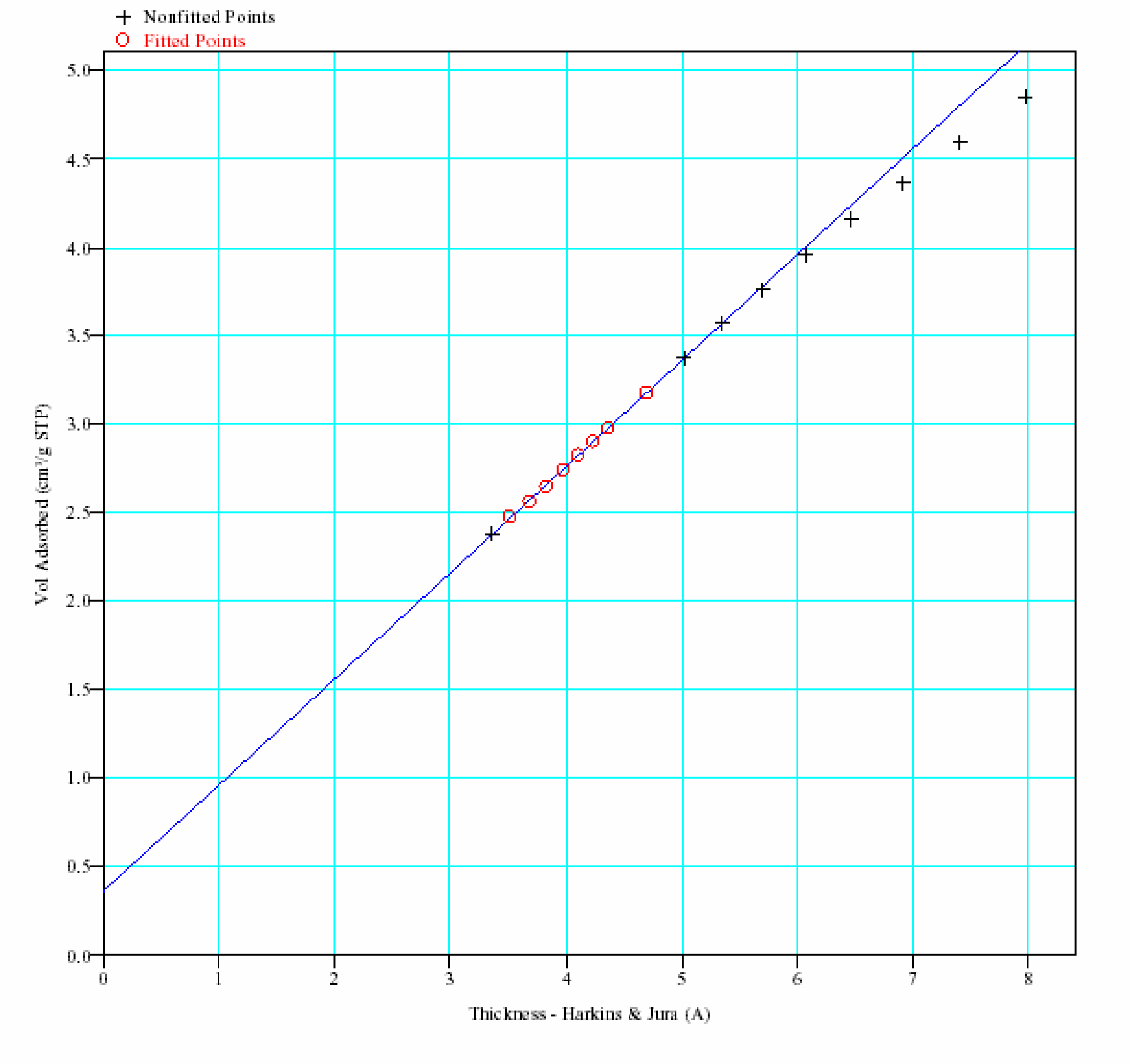
Density Conversion Factor: 0.001547

Total Surface Area (by BET): 10.6310

Relative Pressure	Statistical Thickness (A)	Vol Adsorbed (cm³/g)
0.061847651	3.3553	2.3846
0.080393970	3.5205	2.4728
0.100460239	3.6819	2.5622
0.120513078	3.8315	2.6472
0.140512090	3.9730	2.7366
0.160516346	4.1093	2.8195
0.180661813	4.2429	2.8998
0.200573214	4.3725	2.9768
0.250496782	4.6930	3.1726
0.300890995	5.0180	3.3750
0.351122255	5.3513	3.5743
0.400761137	5.6966	3.7639
0.450579308	6.0658	3.9552

0.500631180	6.4673	4.1576
0.550886666	6.9107	4.3665
0.600721984	7.4022	4.5894
0.650755668	7.9639	4.8480

t-plot:



BJH Adsorption Pore Distribution Report

t = 3.5400 x [-5.0000 / ln(P/Po)]0.3330

Diameter Range: 17.0000 to 3000.0000 A

Adsorbate Property Factor: 9.530000 A

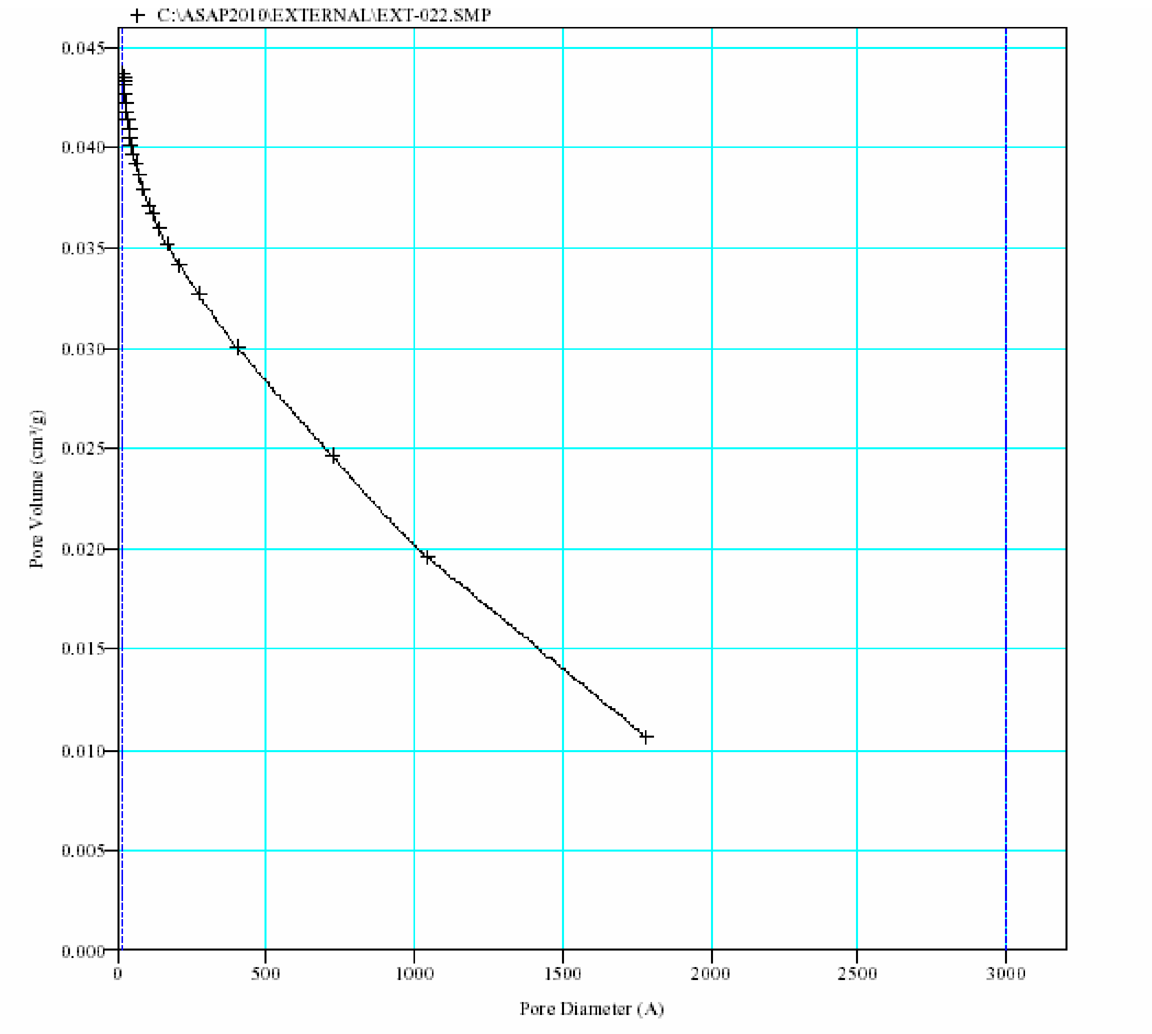
Density Conversion Factor: 0.001547

Fraction of Pores Open at Both Ends: 0.000

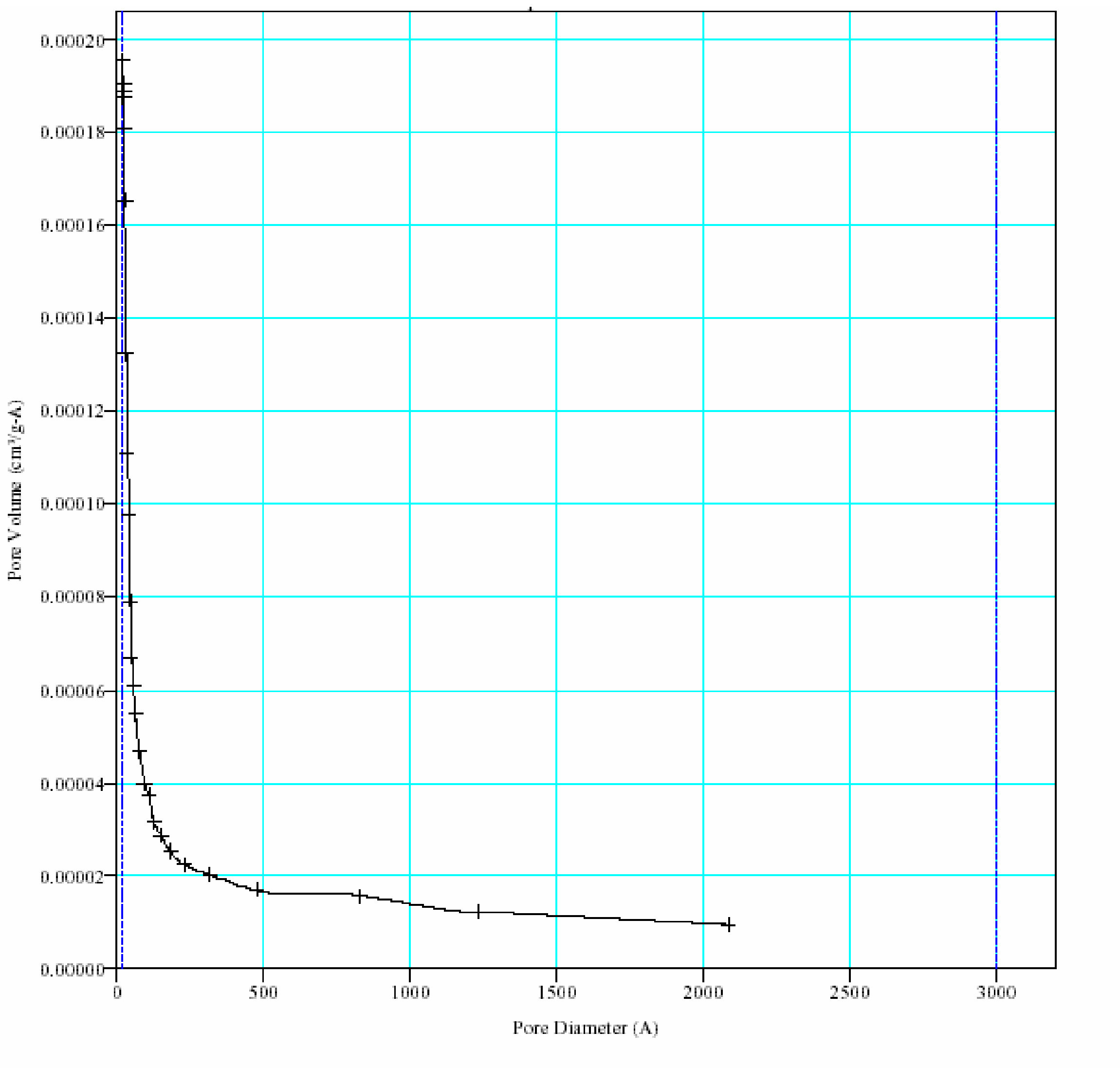
Pore Diameter Range (A)	Average Diameter (A)	Incremental Pore Volume (cm^3/g)	Cumulative Pore Volume (cm^3/g)	Incremental Pore Area (m^2/g)	Cumulative Pore Area (m^2/g)
2891.8-1784.7	2086.7	0.010617	0.010617	0.204	0.204
1784.7-1046.6	1232.1	0.008983	0.019600	0.292	0.495
1046.6- 725.1	827.8	0.005044	0.024644	0.244	0.739
725.1- 402.9	476.1	0.005444	0.030089	0.457	1.196
402.9- 275.1	314.5	0.002590	0.032679	0.329	1.526
275.1- 208.4	232.1	0.001492	0.034170	0.257	1.783
208.4- 167.5	183.2	0.001032	0.035203	0.225	2.008
167.5- 140.5	151.4	0.000773	0.035975	0.204	2.212
140.5- 117.5	126.7	0.000725	0.036700	0.229	2.441
117.5- 105.8	111.0	0.000439	0.037139	0.158	2.599
105.8- 84.9	92.8	0.000836	0.037975	0.360	2.960
84.9- 70.7	76.3	0.000663	0.038638	0.348	3.307
70.7- 60.4	64.6	0.000564	0.039202	0.349	3.656
60.4- 52.5	55.8	0.000479	0.039680	0.343	4.000
52.5- 46.3	49.0	0.000415	0.040096	0.339	4.339
46.3- 41.2	43.4	0.000405	0.040501	0.373	4.712
41.2- 37.0	38.8	0.000417	0.040918	0.430	5.142
37.0- 33.3	34.9	0.000404	0.041322	0.463	5.605
33.3- 30.1	31.5	0.000421	0.041743	0.534	6.140

30.1- 27.3	28.5	0.000475	0.042218	0.667	6.806
27.3- 24.6	25.8	0.000497	0.042715	0.771	7.578
24.6- 22.2	23.2	0.000463	0.043177	0.796	8.374
22.2- 21.3	21.7	0.000170	0.043347	0.313	8.687
21.3- 20.3	20.8	0.000177	0.043524	0.341	9.028
20.3- 19.4	19.8	0.000183	0.043707	0.369	9.397

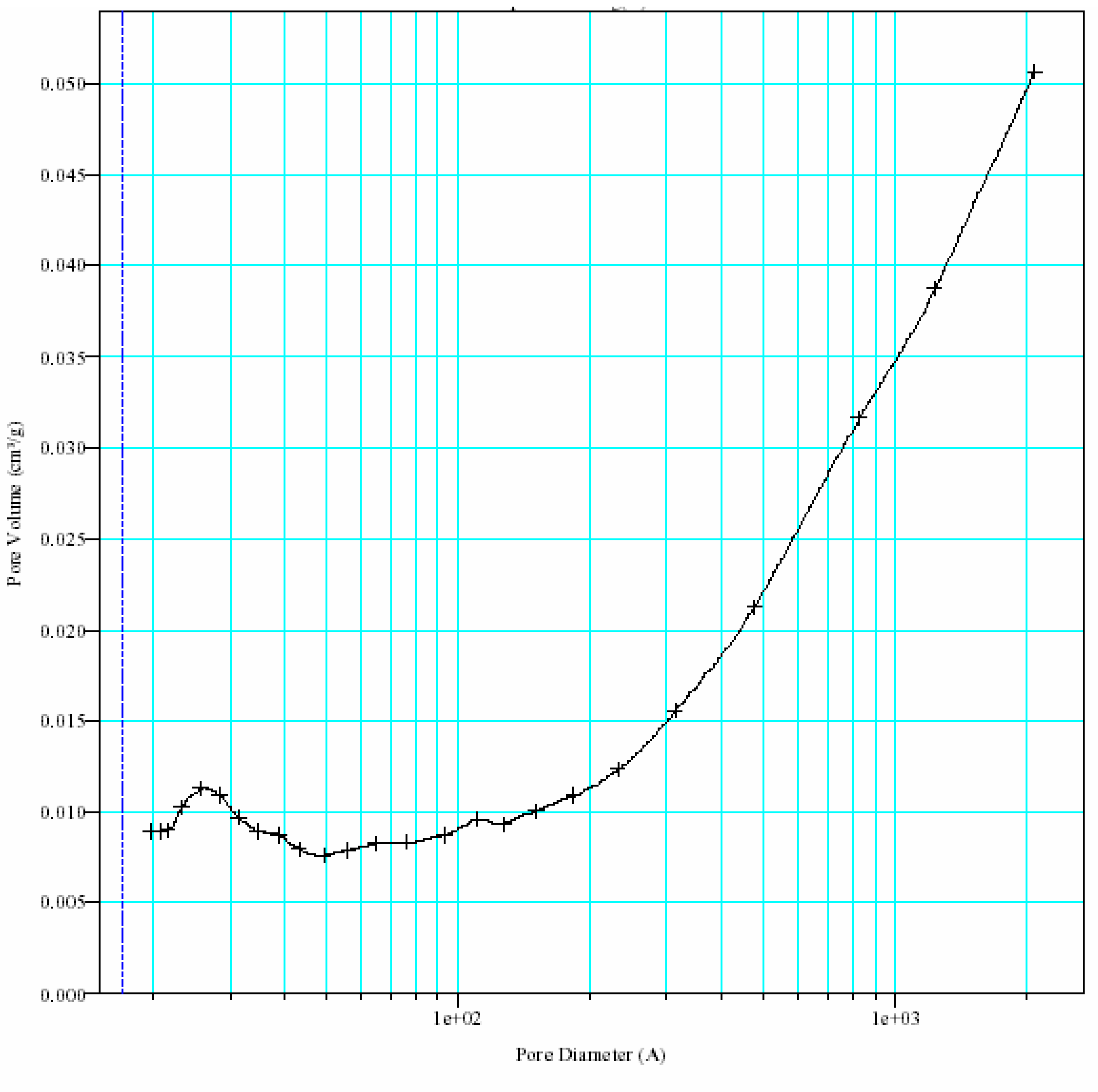
BJH Adsorption Cumulative Pore Volume:



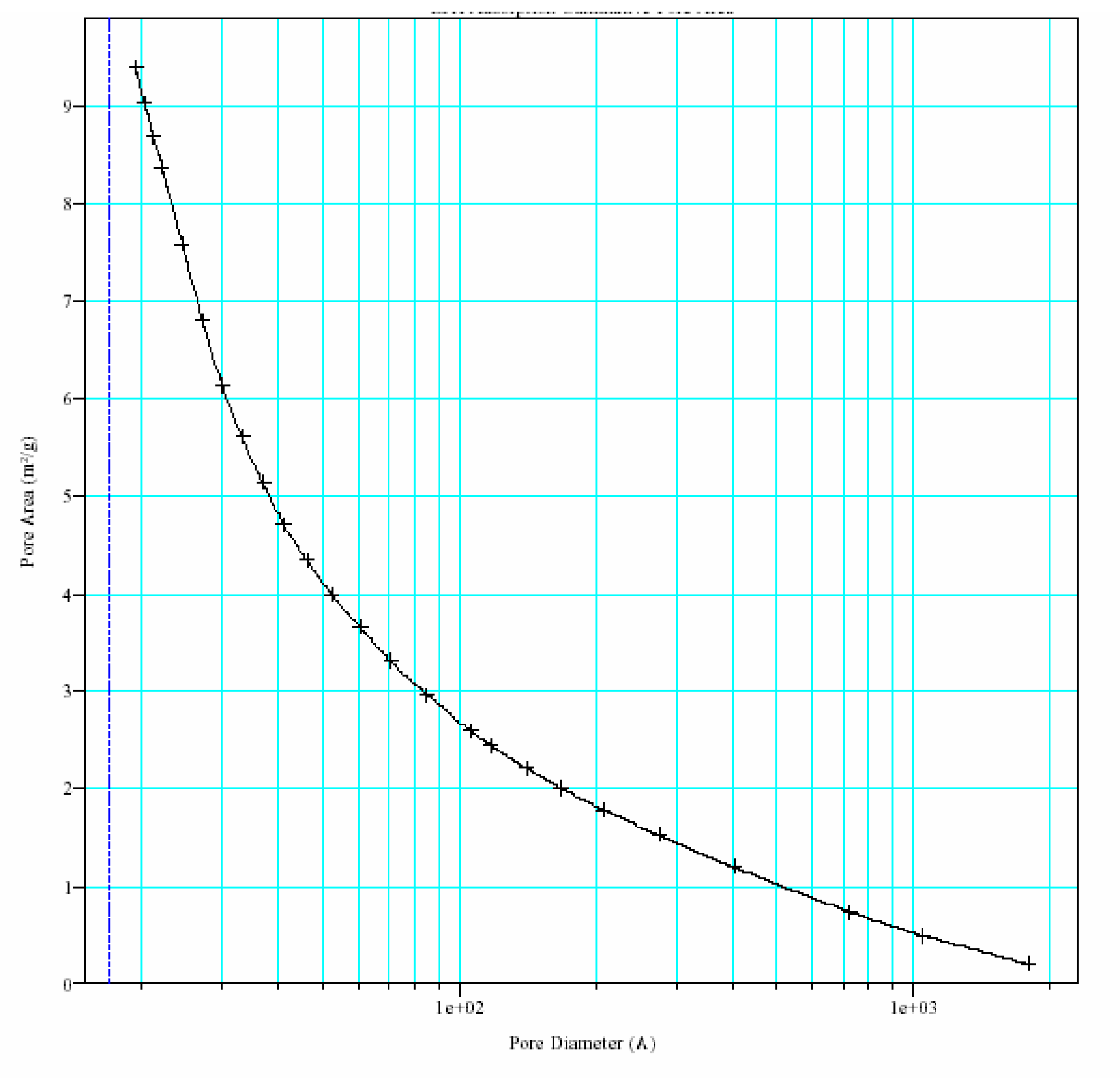
BJH Adsorption dV/dD Pore Volume



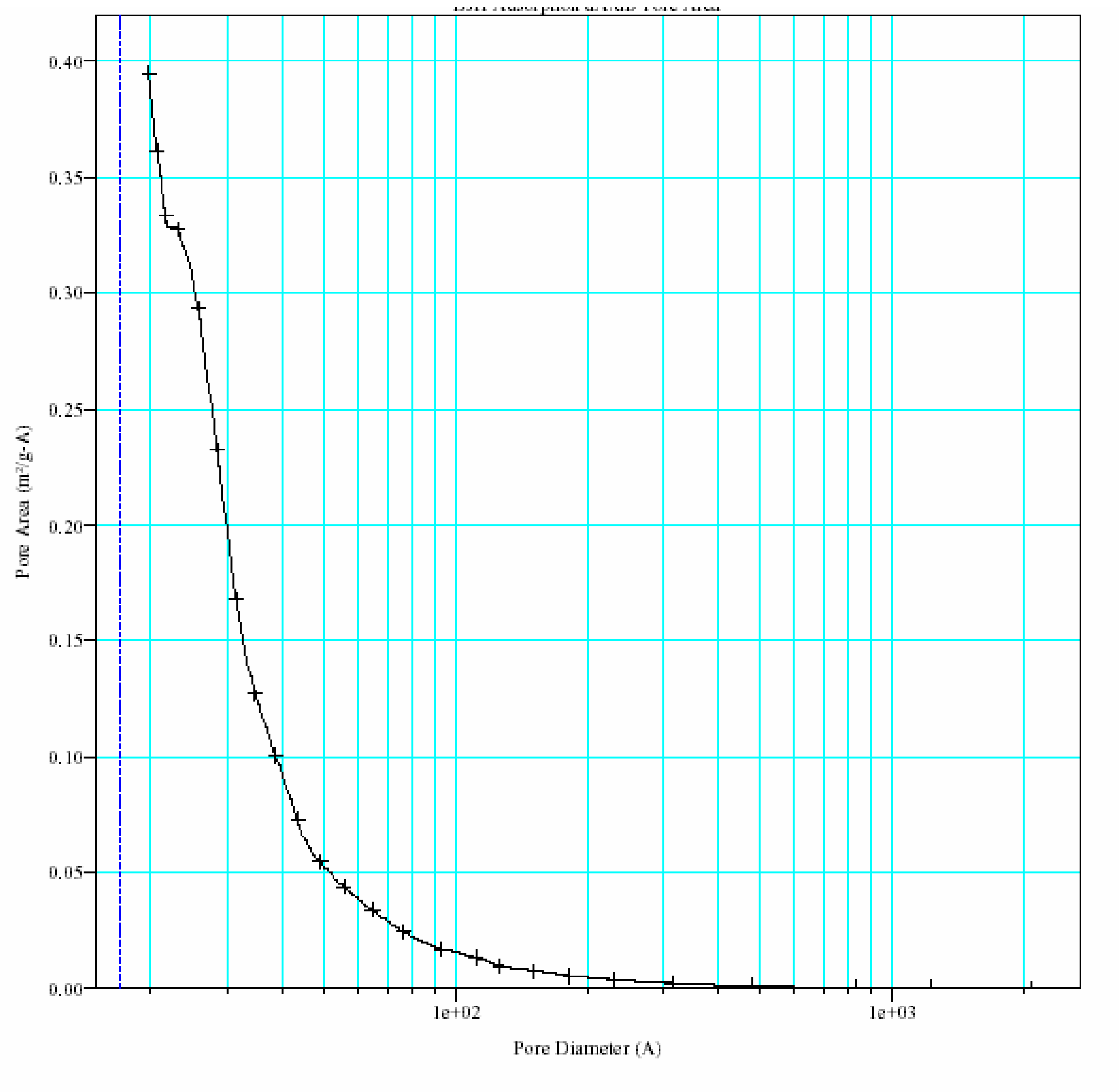
BJH Adsorption dV/dlog(D) Pore Volume



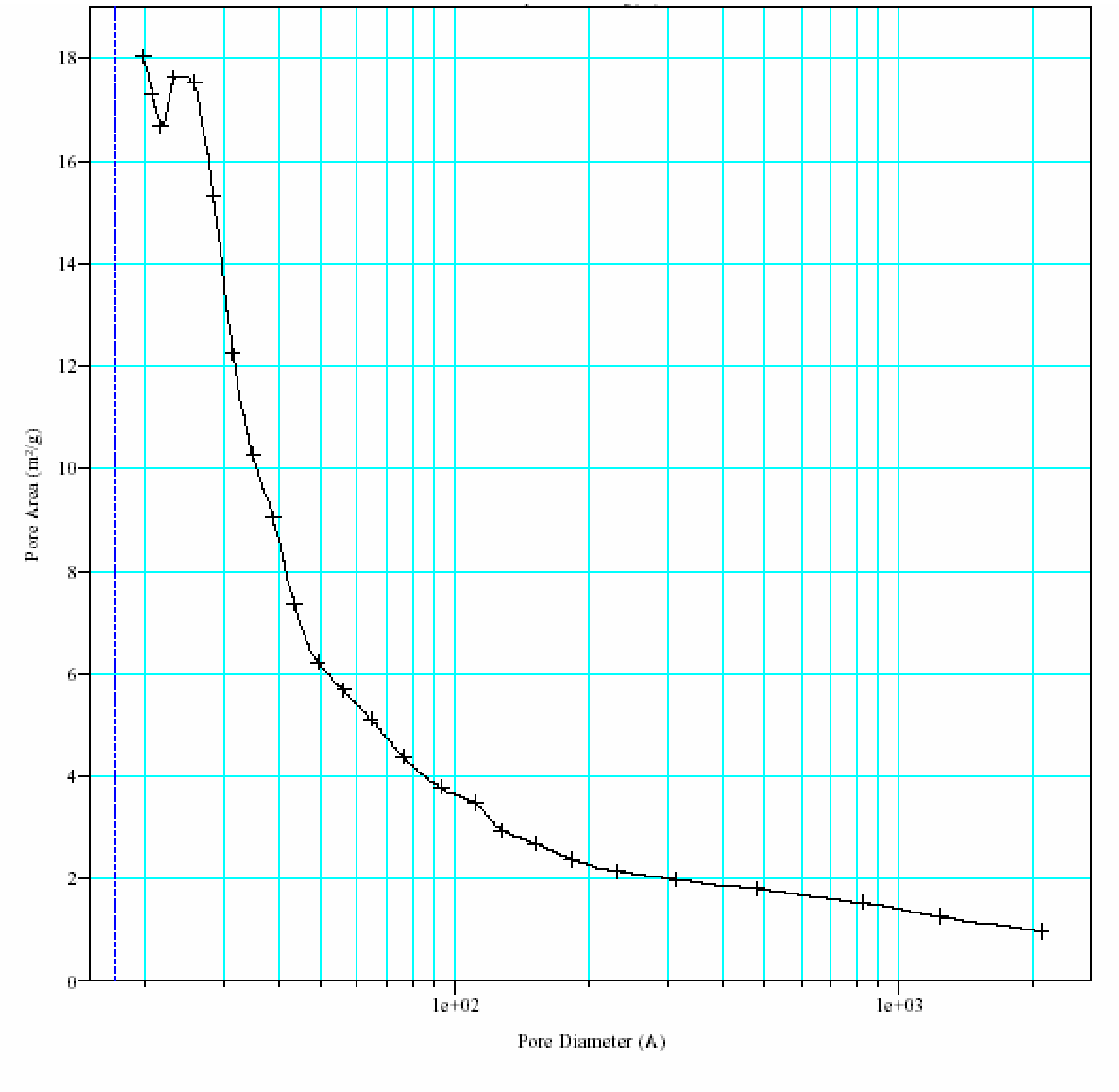
BJH Adsorption Cumulative Pore Area



BJH Adsorption dA/dD Pore Area



BJH Adsorption dA/dlog(D) Pore Area



BJH Desorption Pore Distribution Report

t = 3.5400 x [-5.0000 / ln(P/Po)]0.3330

Diameter Range: 17.0000 to 3000.0000 A

Adsorbate Property Factor: 9.530000 A

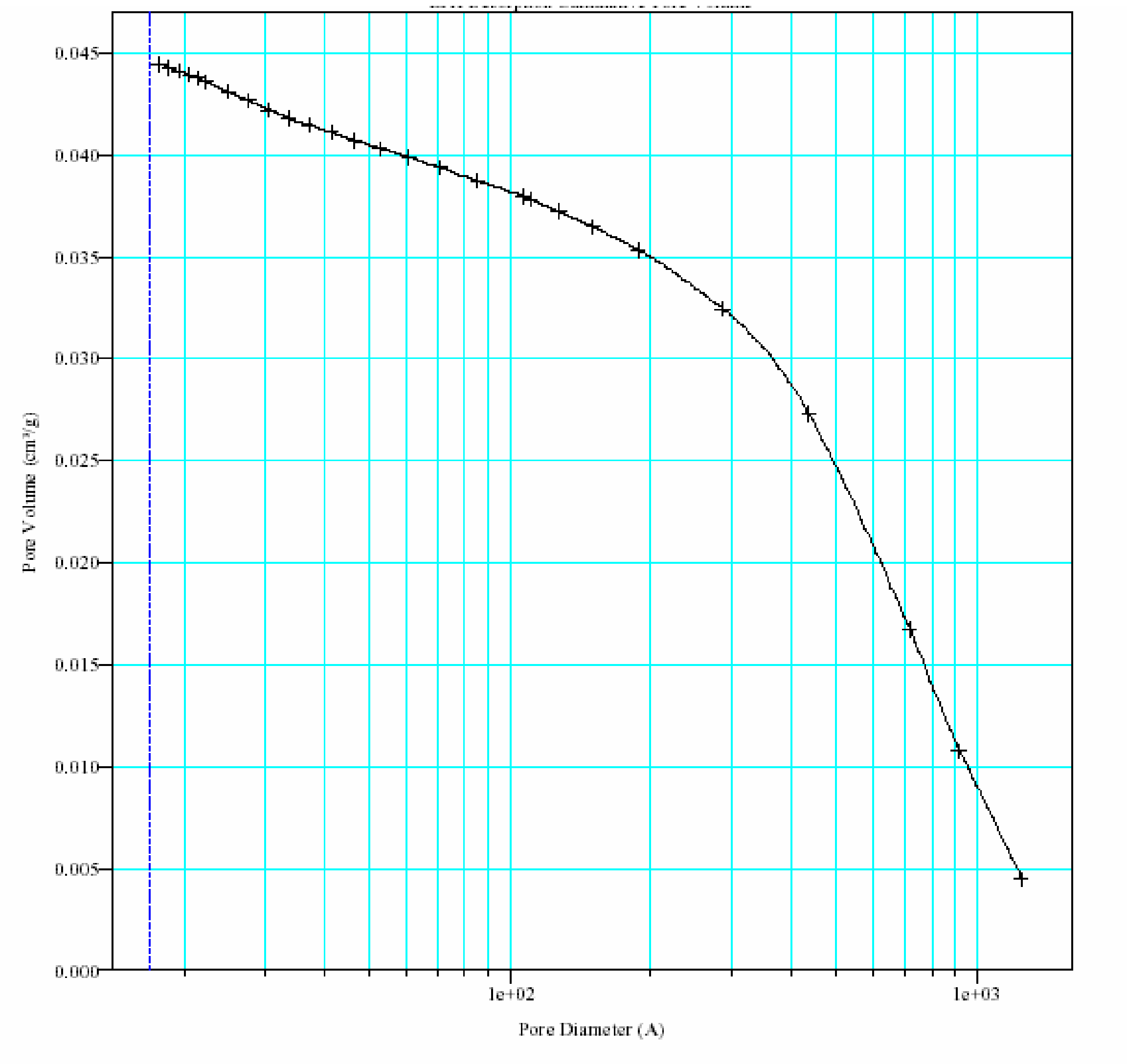
Density Conversion Factor: 0.001547

Fraction of Pores Open at Both Ends: 0.000

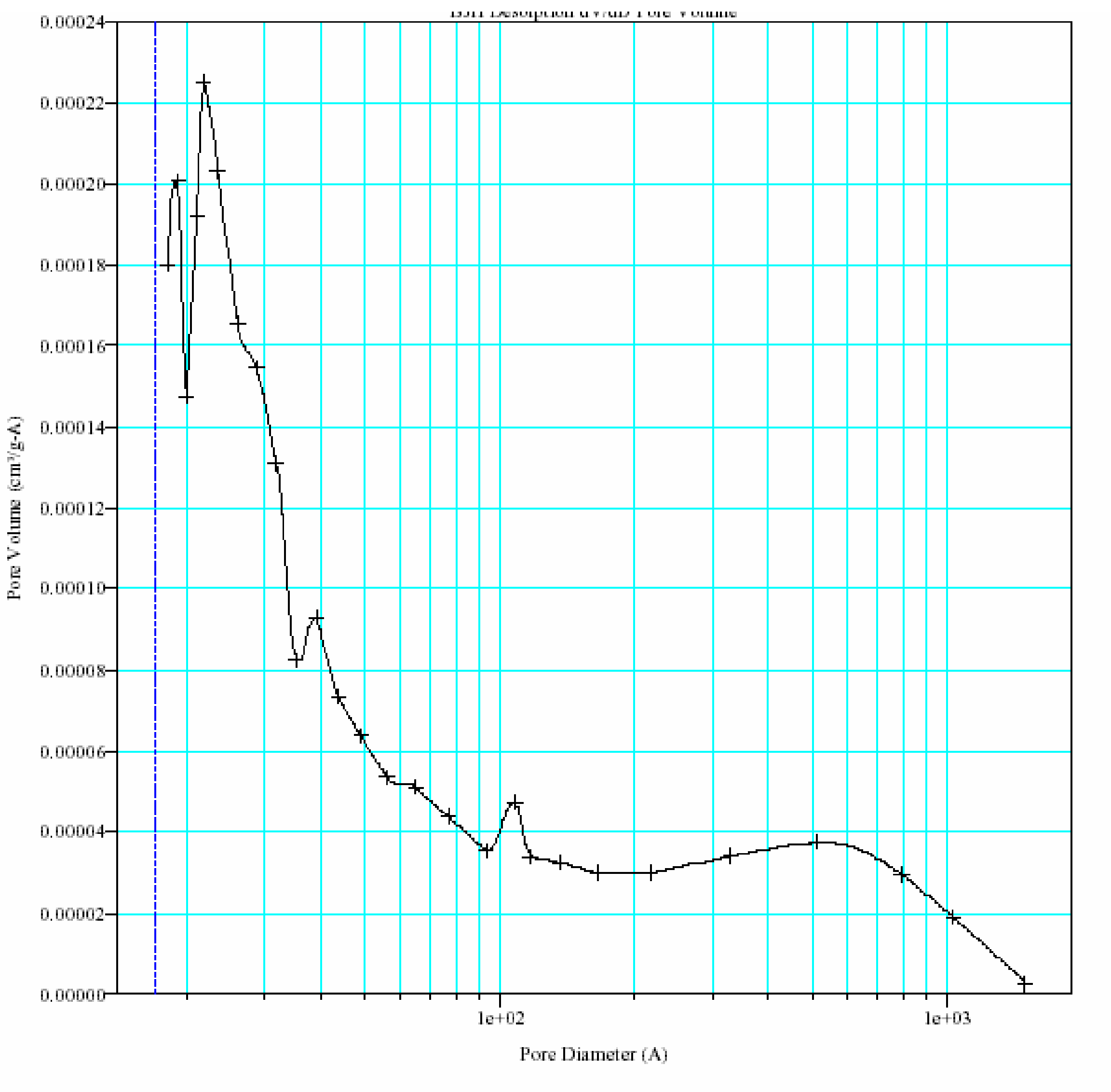
Pore Diameter Range (A)	Average Diameter (A)	Incremental Pore Volume (cm³/g)	Cumulative Pore Volume (cm³/g)	Incremental Pore Area (m²/g)	Cumulative Pore Area (m²/g)
2892.0-1250.0	1501.9	0.004492	0.004492	0.120	0.120
1250.0- 919.6	1034.4	0.006283	0.010775	0.243	0.363
919.6- 719.4	794.6	0.005903	0.016678	0.297	0.660
719.4- 436.6	510.4	0.010604	0.027282	0.831	1.491
436.6- 284.9	328.7	0.005167	0.032449	0.629	2.120
284.9- 188.7	216.8	0.002877	0.035326	0.531	2.650
188.7- 150.3	164.8	0.001157	0.036483	0.281	2.931
150.3- 127.3	136.7	0.000744	0.037227	0.218	3.149
127.3- 110.6	117.7	0.000566	0.037793	0.192	3.341
110.6- 106.6	108.5	0.000189	0.037982	0.070	3.411
106.6- 85.3	93.3	0.000757	0.038739	0.325	3.735
85.3- 70.9	76.6	0.000635	0.039374	0.332	4.067
70.9- 60.5	64.8	0.000533	0.039908	0.329	4.397
60.5- 52.7	55.9	0.000422	0.040330	0.302	4.698
52.7- 46.5	49.1	0.000394	0.040724	0.321	5.019
46.5- 41.4	43.6	0.000376	0.041100	0.346	5.365
41.4- 37.1	39.0	0.000394	0.041494	0.405	5.770
37.1- 33.4	35.0	0.000303	0.041797	0.346	6.116
33.4- 30.3	31.6	0.000417	0.042214	0.527	6.642

30.3- 27.4	28.6	0.000445	0.042659	0.621	7.264
27.4- 24.8	25.9	0.000430	0.043089	0.664	7.928
24.8- 22.4	23.4	0.000493	0.043582	0.843	8.771
22.4- 21.4	21.9	0.000215	0.043797	0.393	9.164
21.4- 20.5	20.9	0.000178	0.043975	0.340	9.504
20.5- 19.5	20.0	0.000138	0.044113	0.276	9.780
19.5- 18.6	19.0	0.000191	0.044304	0.402	10.183
18.6- 17.6	18.1	0.000173	0.044477	0.382	10.565

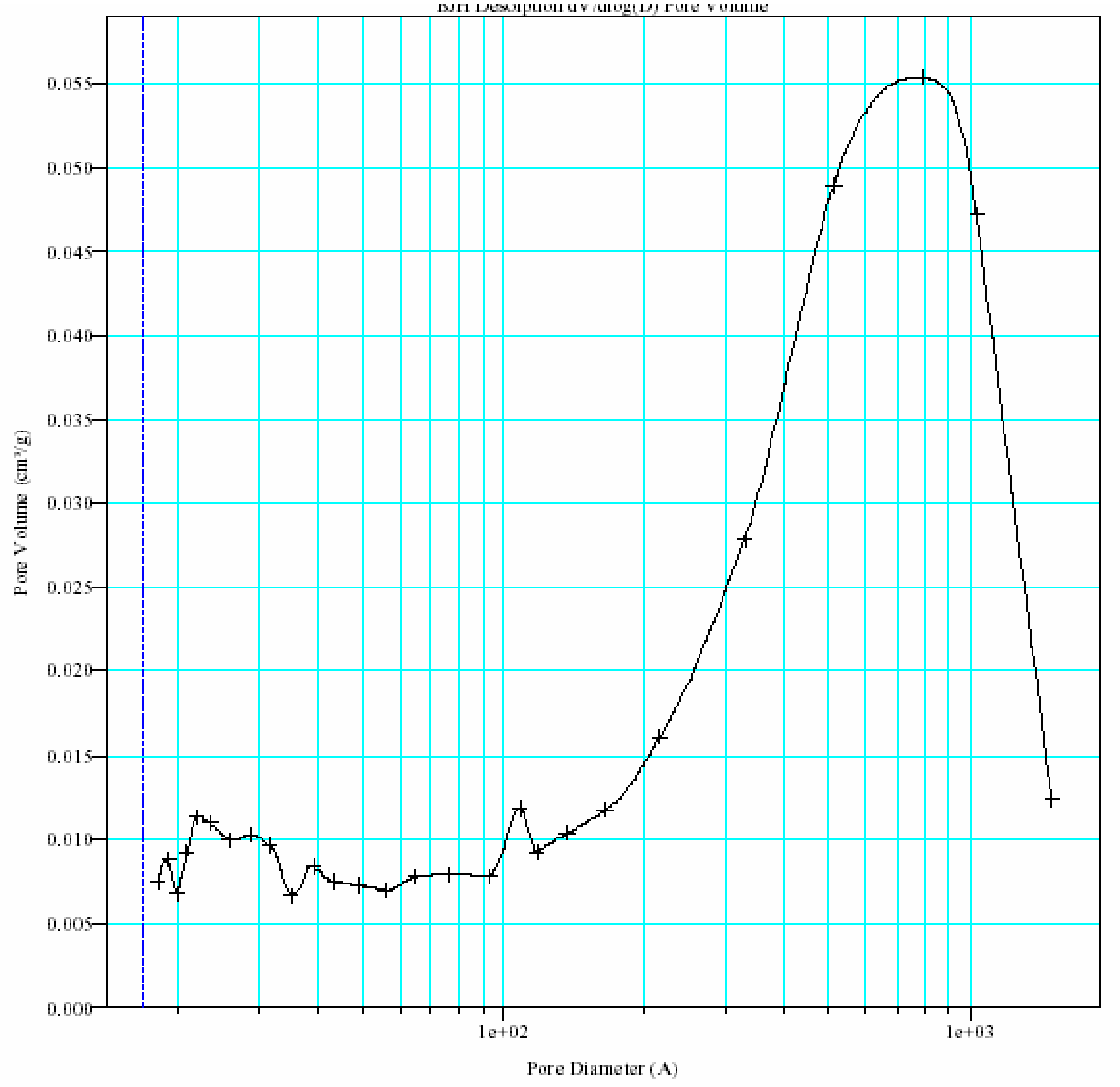
BJH Desorption Cumulative Pore Volume



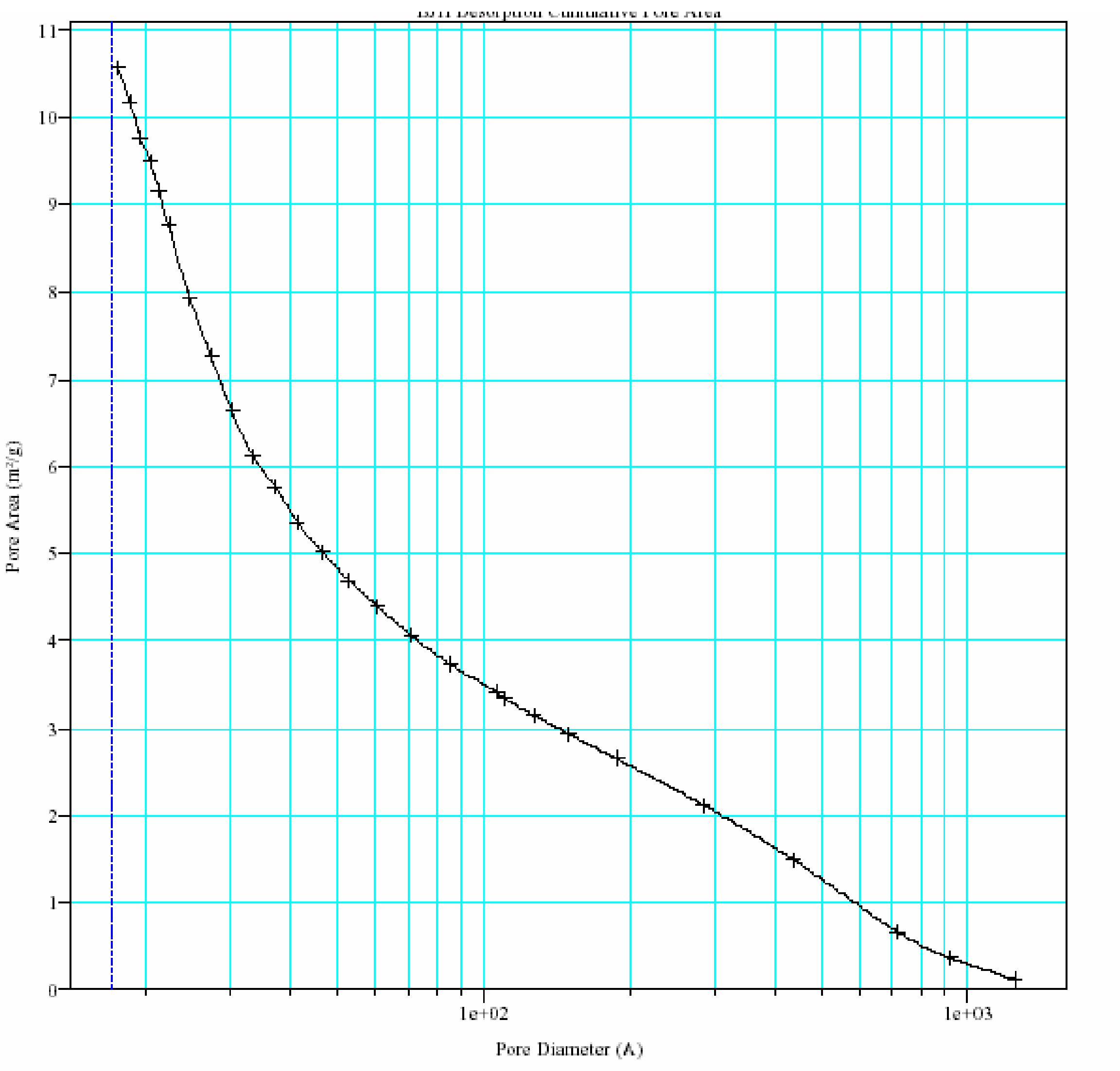
BJH Desorption dV/dD Pore Volume



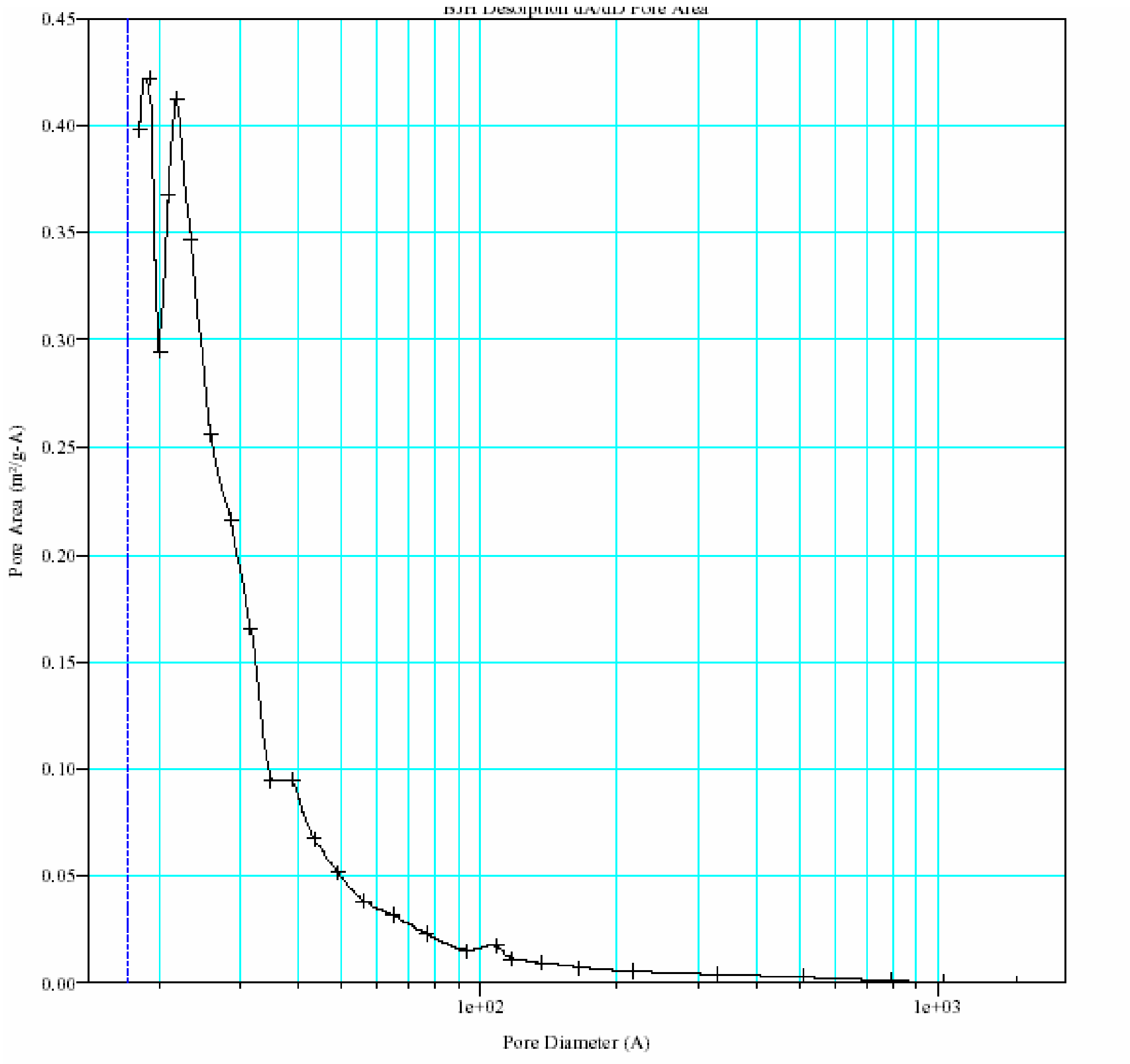
BJH Desorption dV/dlog(D) Pore Volume



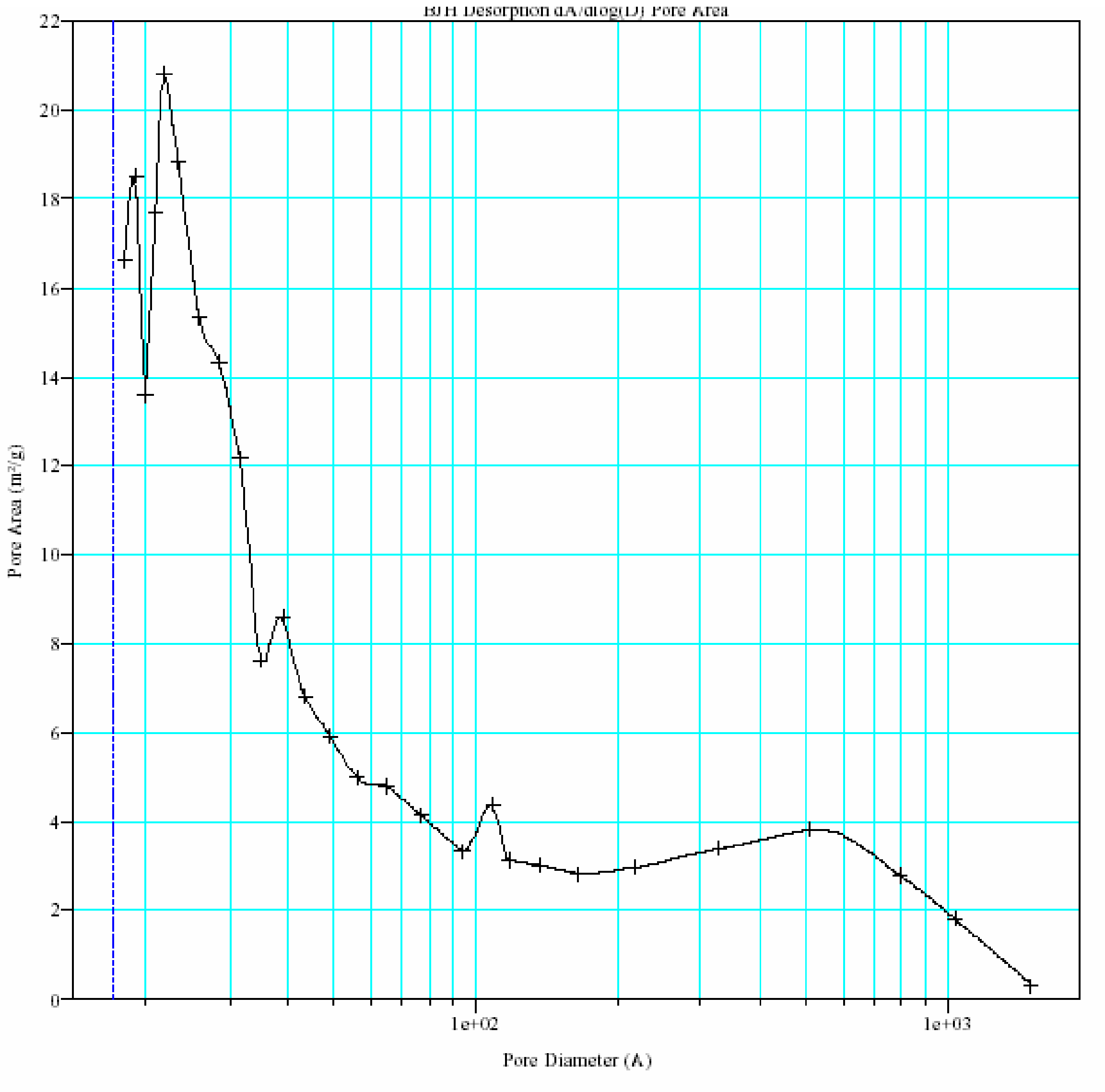
BJH Desorption Cumulative Pore Area



BJH Desorption dA/dD Pore Area



BJH Desorption dA/dlog(D) Pore Area



Summary report:

Area

Single Point Surface Area at P/Po 0.20057321 : 10.3596 m²/g

BET Surface Area: 10.6310 m²/g

Langmuir Surface Area: 14.6248 m²/g

Micropore Area: 1.3536 m²/g

External Surface Area: 9.2774 m²/g

BJH Adsorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 A Diameter: 9.3969 m²/g

BJH Desorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 A Diameter: 10.5651 m²/g

Volume

Single Point Adsorption Total Pore Volume of pores less than 725.0691 A Diameter at P/Po 0.97256591: 0.020724 cm³/g

Micropore Volume: 0.000549 cm³/g

BJH Adsorption Cumulative Pore Volume of pores between 17.000000 and 3000.000000 A Diameter: 0.043707 cm³/g

BJH Desorption Cumulative Pore Volume of pores between 17.000000 and 3000.000000 A Diameter: 0.044477 cm³/g

Pore Size

Adsorption Average Pore Diameter (4V/A by BET): 77.9770 A

BJH Adsorption Average Pore Diameter (4V/A): 186.0485 A

BJH Desorption Average Pore Diameter (4V/A): 168.3933 A