ALUMINA SILICON OXYCARBIDE HYBRIDS

Thesis submitted in partial fulfillment as a requirement for the degree of Bachelor of Technology under the guidance of Professor SHANTANU KUMAR BEHERA

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<u>CERTIFICATE</u>

This is to certify that the thesis entitled, "**Alumina silicon oxycarbide hybrids**", submitted by **Mr. Asutosh   Mahapatra (Roll no. 110CR0099)** in partial fulfilment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

Date: 11.05.2013

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<u>ACKNOWLEDGEMENT</u>

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ABSTRACT

Alumina-silicon oxycarbide (from polyphenylmethlsilsesquioxane which is fired in absence of air)batch is synthesized using propanol solution and magnetic stirring. Three batches of different composition are made, ,polyphenylmethylsilsesquoxane being the major constituent (i.e-70:30;80:20;90:10). The polymer will form a coating on the alumina surface. To ensure coating of the alumina surface, polyphenylmethylsilsesquioxane is added first and it is then allowed to dissolve completely by stirring for 15-20 minutes. Then the required amount of alumina is added gradually to the polyphenylmethylsilsesquioxane solution and stirred vigorously for next 20-25 minutes and ensure its complete solution. The powder is pyrolysed at 400˚C, 500˚C,600˚C,800˚C and 900˚C. After the pyrolysis, the overall volume of the composite decreases and the composite becomes more dense.Then characterization of the pyrolysed powder is done by XRD, BET and UV-VIS Spectroscopy.BET was done to study the pore size/volume and surface area of these hybrid. UV-VIS spectroscopy was performed to study the preliminary adsorption properties of these hybrids for toxic ion removal.

CHAPTER-1

INTRODUCTION

1.1 INTRODUCTION:

Porous ceramics containing tailored porosity exhibit special properties and features that usually cannot be achieved by their conventional dense counterparts. Thus, porous ceramics find nowadays many applications as final products and in several technological processes. Porous ceramics are of significant interest due to their wide applications in high-temperature filters, thermal gas separation, lightweight structural components and thermal structural materials. Various fabricating methods are adopted to produce highly porous ceramics which includes the replication of polymer foams by ceramic dip coating, the foaming of aqueous ceramic powder suspensions, the pyrolysis of preceramic precursors, partial sintering by pressureless sintering, and the firing of ceramic. Often for porous ceramics used in high temperature environment, they require high temperature melting point, high mechanical strength, low thermal conductivity, open pore structure and special pore distribution. powder compacts with pore-forming fugitive phases. Changes in open and closed porosity, pore size distribution and pore morphology can have a major effect on a material's properties. All of these microstructural features are in turn highly influenced by the processing route used for the production of the porous material.

Porous bulk ceramics are widely used for industrial applications such as liquid or gas filters, catalysis supports, gas distributors, preforms for metal-impregnated ceramic–metal composites, and implantable bone scaffolds.

Preceramic polymers were proposed as precursors for the fabrication of mainly Si-based advanced ceramics, generally denoted as polymer-derived ceramics (PDCs). From the processing point of view, preceramic polymers have been used as reactive binders to produce technical ceramics, they have been manipulated to allow for the formation of ordered pores in the meso-range, they have been tested for joining advanced ceramic components, and have been processed into bulk or macroporous components.

Alumina is a versatile material used as refractory, engineering ceramics material, abrasive and in various other applications where chemical inertness coupled with its high hardness and abrasiveness is of primary importance.

The term silsesquioxanes in this review refers to all structures with the empirical formulas $RSiO_{3/2}$ where R is hydrogen or any alkyl, alkylene, aryl, arylene, or organo-functional derivatives of alkyl, alkylene, aryl, or arylene groups.

In **polyphenylsilsesquioxane,** the substituent on the silicon atom is a phenyl group, and it is generally characterized by its high thermal stability. **Polyphenylsilsesquioxane has been often referred as a ladder polymer since** Brown et aL6 reported the polymer to have cis-syndiotactic conformation as shown in Figure 1.
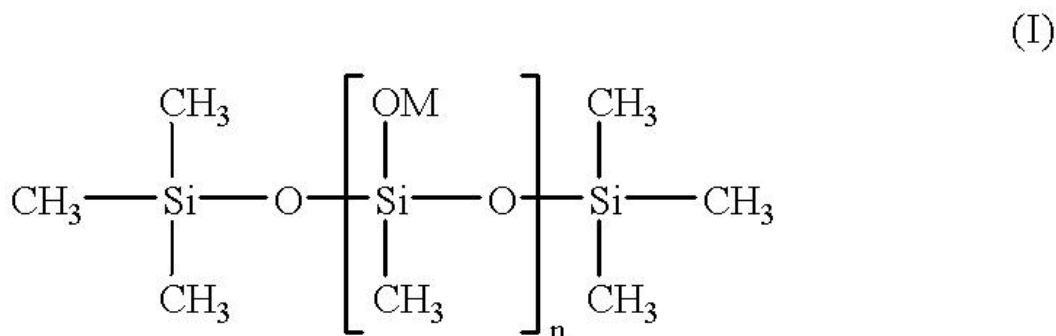
(I)

Figure-1

Frye and Klosowski strongly opposed the linear double chain ladder structure and suggested a more or less randomly linked array of polycyclic cages as shown in figure 2.
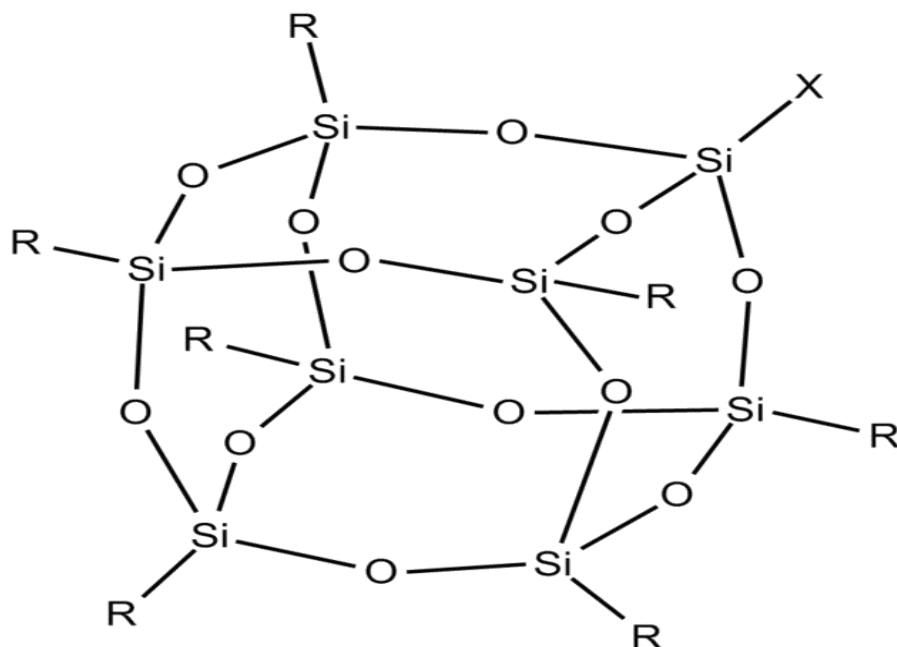
Figure-2

the use of **polyphenylsilsesquioxane** is focused on coatings,particularly in electronics and optical devices. Among these, the application in photoresists is outstanding.Applications for interlayer dielectrics and protective coating films for semiconductor device liquid crystal display element magnetic recording media,and optical fiber coatings are disclosed. Other applications include their use in gas separation membrane, binders for ceramics and carcinostatic drugs.

In this experiment, the polymer is expected to form a coating on the alumina surface on which pore anlaysis would be done. The basic idea for forming a coating on the oxide ceramic is to increase the specific surface area of the material . In recent years, research has been focused on the composite powders consisting of Al_2O_3 powder coated with minor chemical constituents. The main advantages of the coating processing are to improve the dispersability of the powders , control interfacial properties (hydrophilic/hydrophobic surface), modify the colloidal behavior of powders, introduce a uniform incorporation of minor additives, and/or prepare a composite powder for the purposes of sintering aid, microstructure control, and desired functional properties.A commercially viable PDC can be prepared by using a ceramic oxide and precursors containing siloxane or siliconoxycarbide.Then the pyrolysis of this mixture is expected to form a di-phasic material containing either SiO_2 (in air) or amorphous SiOC (in absence of air).Absorption of organic dyes (THYMMOL BLUE) have been evaluated and a material having very close specific surface area to that of alumina is obtained.

CHAPTER-2

LITERATURE REVIEW

G. L. Messing et al [5],Mullite in a diphasic mixture consisting of a preceramic polymer filled with alumina nanoparticles was investigated and The key findings are the addition of nanosized fillers to preceramic polymers allows to obtain mullite ceramics at a low temperature, with very favorable kinetics and a high degree of microstructural control on the crystalline phase assemblage. In our experiments, we never observed any evidence of the formation of Spinel suggesting that the mechanism of mullite formation could be similar to that

reported by Huling and Messing, which involves the release of Al from α-alumina. The slightly lower energy barrier for the nucleation and growth of mullite in our system is clearly attributable to the synergy between the high specific surface of nanosized g-alumina particles used as fillers and the highly reactive silica derived from the silicone pyrolysis. It should be highlighted that MK silicone is known to yield, on treatment in an inert atmosphere (from a temperature of about 500°C, but more often at temperatures exceeding 1000° c). It is reasonable to suppose that also the Si–CH$_3$ bonds that break via oxidation at high temperatures would lead to ''reactive'' Si atoms. These reactive centers would facilitate an easier interaction with nanometric gama-alumina, leading to mullite, which is based on interdiffusion of aluminum, silicon, and oxygen atoms at a submicrometer scale.

Silsesquioxanes consist of a silicon-oxygen framework with attached functionality groups in the forms of pendants, so named due to each silicon atom being bound to 1.5 oxygen atoms (on average) and one R group. The general formula for this type of molecule is (RSiO1.5)n, where R represents the pendant group. Generally R can be a wide range of functionalities, either a hydrogen or organic group including; alcohols, esters, phenyl, aryl, methyl, vinyl, alkyl or any of their derivatives **(Ribeiro do Carmo et al ,2006; Striolo et al ,2005;Provatas et al ,1997; Baney et al 1995; Li et al, 2001)**.

Due to the molecules ability to have a wide range of incorporated functionalities it has been found that a high level of compatibility with other materials can be achieved such as with polymers, biological systems and surfaces. This has also led to the ease of modification of the molecule, with the allowed tailoring the material can be suitable for a wide range of applications **(Soong et al, 2007; Li et al 2001; Baney et al 1995).**

Alumina (Al$_2$O$_3$) has wide application as engineering ceramic material due to its high hardness value. It has high melting point (2054 °C), low thermal expansion and high compressive strength which provides good thermal shock resistance [5]. Alumina has good electrical insulation at high

temperatures, good wear resistance and high hardness, makes it suitable for components such as ball valves, piston pumps and deep drawing tools. For machining and grind of alumina diamond tools are needed. Alumina can be used in pure form and also in alloying component in aluminum oxide based ceramics which contain greater than 85% Al_2O_3. Commonly, the green density effects the sintering of the product. The green density can be controlled with pressure in powder pressing.The organic-inorganic microstructure gives the Silsesquioxanes properties intermediate of ceramics and polymers, hence being classed as a hybrid material. Enhancements in thermal and thermomechanical stability, fire retardant properties, dielectric constant, optical transparency and mechanical toughness are a few of the reported when compared to that of the single materials (**Xu et al, 2001; Aldrich, 2001**). By combining the two classes of materials in the hybrid nature of Silsesquioxanes it is hoped that the most beneficial properties of the each can be tailored into one material, such as the processability, toughness and cost of polymers with the thermal and oxidative stability of ceramics (**Schwab and Lictenhan, 1998**). The properties are due to the unique molecular structures which can be formed, depending on production method, with belief that with differing species differing lead properties can be seen (**Li et al,2001**).(**Anran Guo, Martina Roso, Michele Modesti, Jiachen Liu, Paolo Colombo et al,2013**)Table II reports the solubility of MK, H44 and PVP in some common solvents.

SOLUTE	isopropanol	DMF	Acetone	Ethanol	Chloroform
MK	High	Insoluble	Partial	Partial	Partial
H44	High	High	Partial	Partial	Partial

CHAPTER-3

EXPERIMENTAL PROCEDURE

3 EXPERIMENTAL WORK

Raw material was taken from microcrystalline alumina (sourced from TRL) **and Si**lres **H44.**

3.1 BATCH PREPARATION AND ITS PYROLYSIS

Microcrystalline alumina (sourced from TRL) is taken and weighed for the required amount and Wacker silres H44 is taken and weighed .then the taken amount of H44 is added to 20 ml of propanol in a beaker and it is magnetically stirred for 25-30 minutes until gets completely dissolved. Then gradually the taken amount of alumina is added to the solution and stirred magnetically to facilitate coating of H44 on the alumina surface. Then, it is pyrolysed at 500^0 c, 600^0 c, 800^0 c and 900^0 c.

3.2 7(H44):3(Al$_2$O$_3$) BATCH PREPARATION

7g of Wacker silres H44 is taken and added to 20 ml of propanol and then it is magnetically stirred for 25-30 minutes until it gets completely dissolved. Then gradually, 3g of microcrystalline alumina sourced from TRL is added to the solution to facilitate coating of H44 on the alumina surface. Then, it is pyrolysed at 500^0 c, 600^0 c, 800^0 c and 900^0 c.
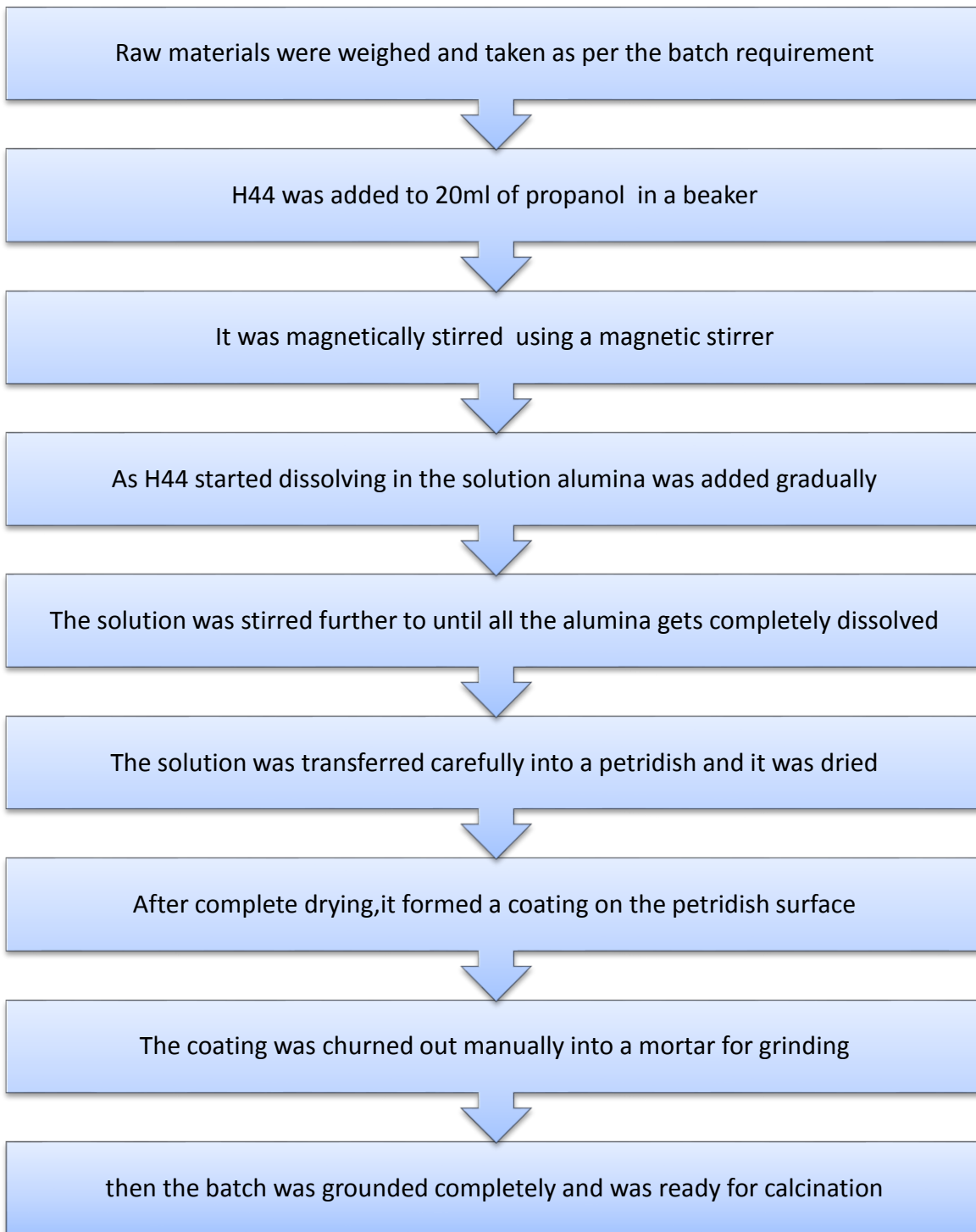
3.3 8(H44):2(Al$_2$O$_3$) BATCH PREPARATION

8g of Wacker silres H44 is taken and added to 20 ml of propanol and then it is magnetically stirred for 25-30 minutes until it gets completely dissolved. Then gradually, 2g of microcrystalline alumina sourced from TRL is added to the solution to facilitate coating of H44 on the alumina surface. Then, it is pyrolysed at 500^0 c, 600^0 c, 800^0 c and 900^0 c.

3.4 9(H44):1(Al$_2$O$_3$) BATCH PREPARATION

9g of Wacker silres H44 is taken and added to 20 ml of propanol and then it is magnetically stirred for 25-30 minutes until it gets completely dissolved. Then gradually, 1g of microcrystalline alumina sourced from TRL is added to the solution to facilitate coating of H44 on the alumina surface. Then, it is pyrolysed at 500^0 c, 600^0 c, 800^0 c and 900^0 c.

Raw materials were weighed and taken as per the batch requirement

H44 was added to 20ml of propanol in a beaker

It was magnetically stirred using a magnetic stirrer

As H44 started dissolving in the solution alumina was added gradually

The solution was stirred further to until all the alumina gets completely dissolved

The solution was transferred carefully into a petridish and it was dried

After complete drying,it formed a coating on the petridish surface

The coating was churned out manually into a mortar for grinding

then the batch was grounded completely and was ready for calcination

CHAPTER-4

CHARACTERIZATION

4.1 XRD ANALYSIS

The presence of alumina phase in the used powder is known from the X-ray diffraction measurement of powder. When X-rays passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation as shown in Figure 3.1. For crystalline materials the distances between the planes is same and if the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur. This diffraction where X-rays are emitted at characteristic angles based on the spaces between the atoms organized in crystalline structures are called planes. XRD plot was obtained from 20^0 to 80^0 at a scanning rate of 20^0/min.
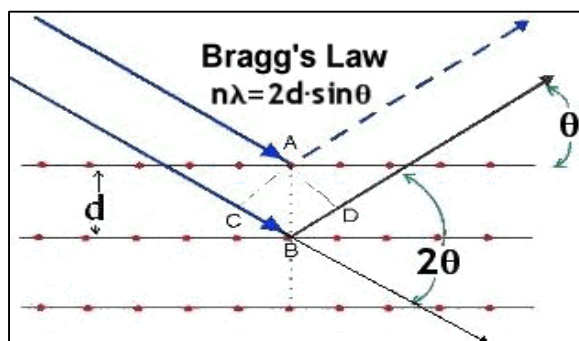
Figure 4.1: Study of crystallographic plane during XRD

4.2 Brunauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) Pore Size and Volume Analysis

BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2/g yielding important information in studying the effects of surface porosity and particle size in many applications.

BJH analysis can also be employed to determine pore area and specific pore volume using adsorption and desorption techniques. This technique characterises pore size distribution

independent of external area due to particle size of the sample. Specific surface area determinations measuring the external surface area and open pores of macroporous and mesoporous materials, along with pore volume and area distributions that characterize porosity below the effective range of mercury intrusion porosimetry are techniques that can be especially useful for studies of artificial bone materials, catalysts, particle and gas filtration, fuel cell technology, absorbents, sintering studies, zeolites and reactivity studies of materials among a variety of other applications. The flow technique uses a TCD detector to obtain information on the amount of adsorbed gas resulting in a specific BET surface area and/or total pore volume. The volumetric technique provides more information, since many adsorption and/or desorption points are measured providing a full isotherm with information on BET surface area, pore volume and pore size distribution.

4.3 ULTRAVIOLET-VISIBLE SPECTROSCOPY (FOR ADSORPTION EFFICIENCY)

Ultraviolet–visible spectroscopy or **ultraviolet-visible spectrophotometry** (**UV-Vis** or **UV/Vis**) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state. Solutions of transition metal ions can be colored (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another. The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption (λ_{max}).

BEER-LAMBERT'S LAW

The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer-Lambert law:

$$A = \log_{10}(I_0/I) = \epsilon c L,$$

where *A* is the measured absorbance, in **A**bsorbance **U**nits (**AU**), I_0 is the intensity of the incident light at a given wavelength I is the transmitted intensity, *L* the pathlength through the sample, and *c* the concentration of the absorbing species. For each species and wavelength, ε is a constant known as the molar absortivity. This constant is a fundamental molecular property in a given solvent, at a particular temperature and pressure, and has units of $1/M * cm$ or often $AU/M * cm$. The absorbance and extinction ε are sometimes defined in terms of the base-10 logarithm. The Beer-Lambert Law is useful for characterizing many compounds but does not hold as a universal relationship for the concentration and absorption of all substances. A 2nd order polynomial relationship between absorption and concentration is sometimes encountered for very large, complex molecules such as organic dyes.so, the efficiency can be calculated as:
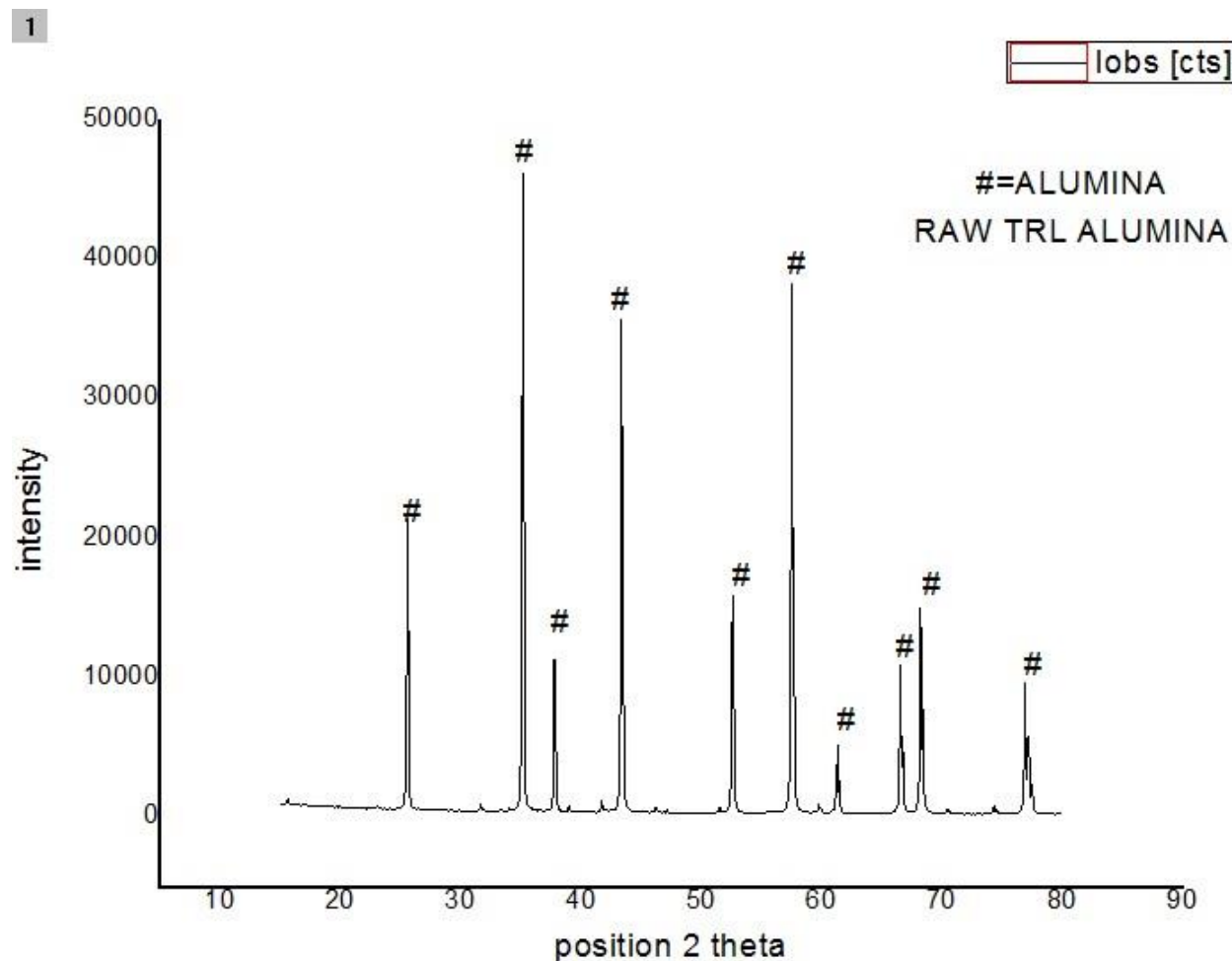
$$A = \left\{ \frac{C_0 - C_e}{C_e} \right\} * 100\%$$

Where, $C_0 = standard\ solution\ concentration;\ A = absorption\ efficiency;\ C_e = concentration\ of\ a\ particular\ solution.$
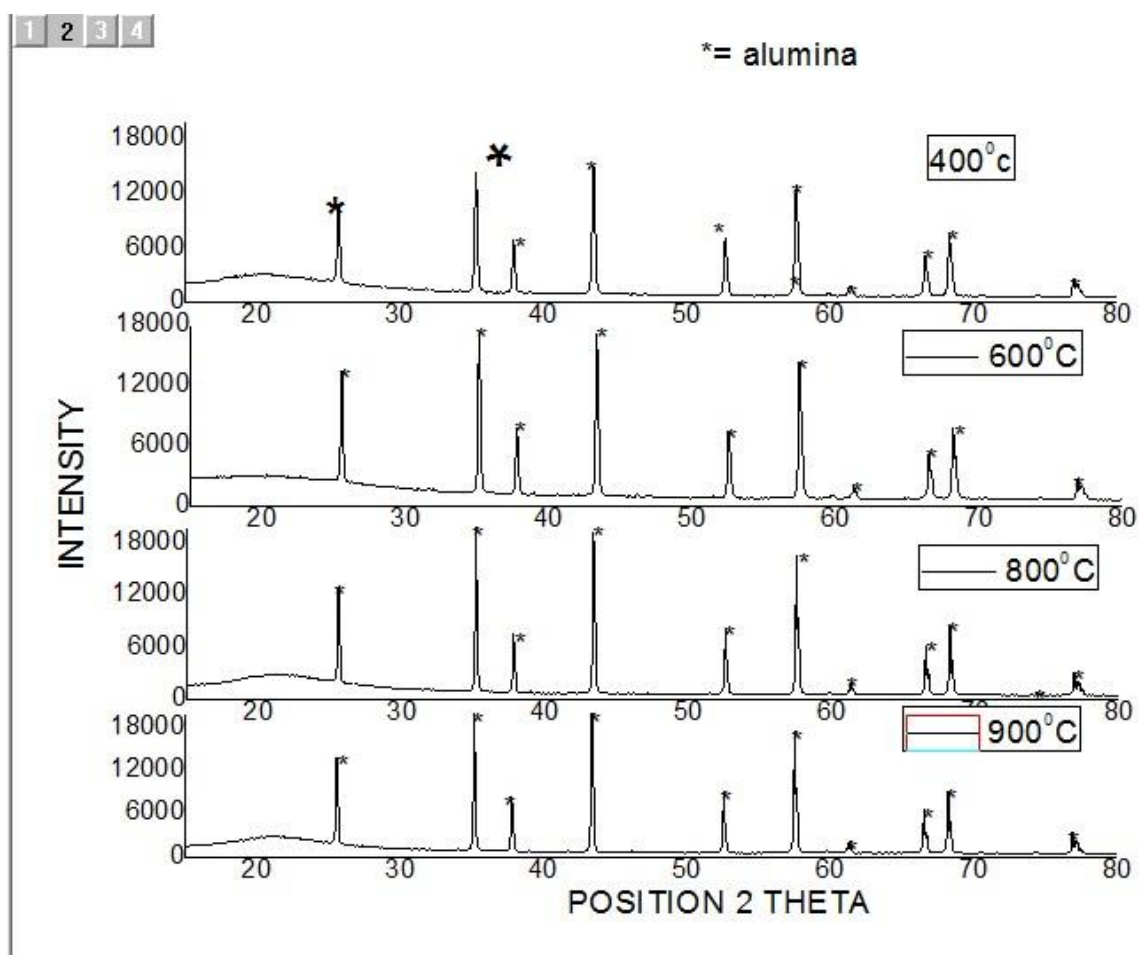
CHAPTER-5

RESULTS & DISCUSSIONS

5.1 XRD ANALYSIS

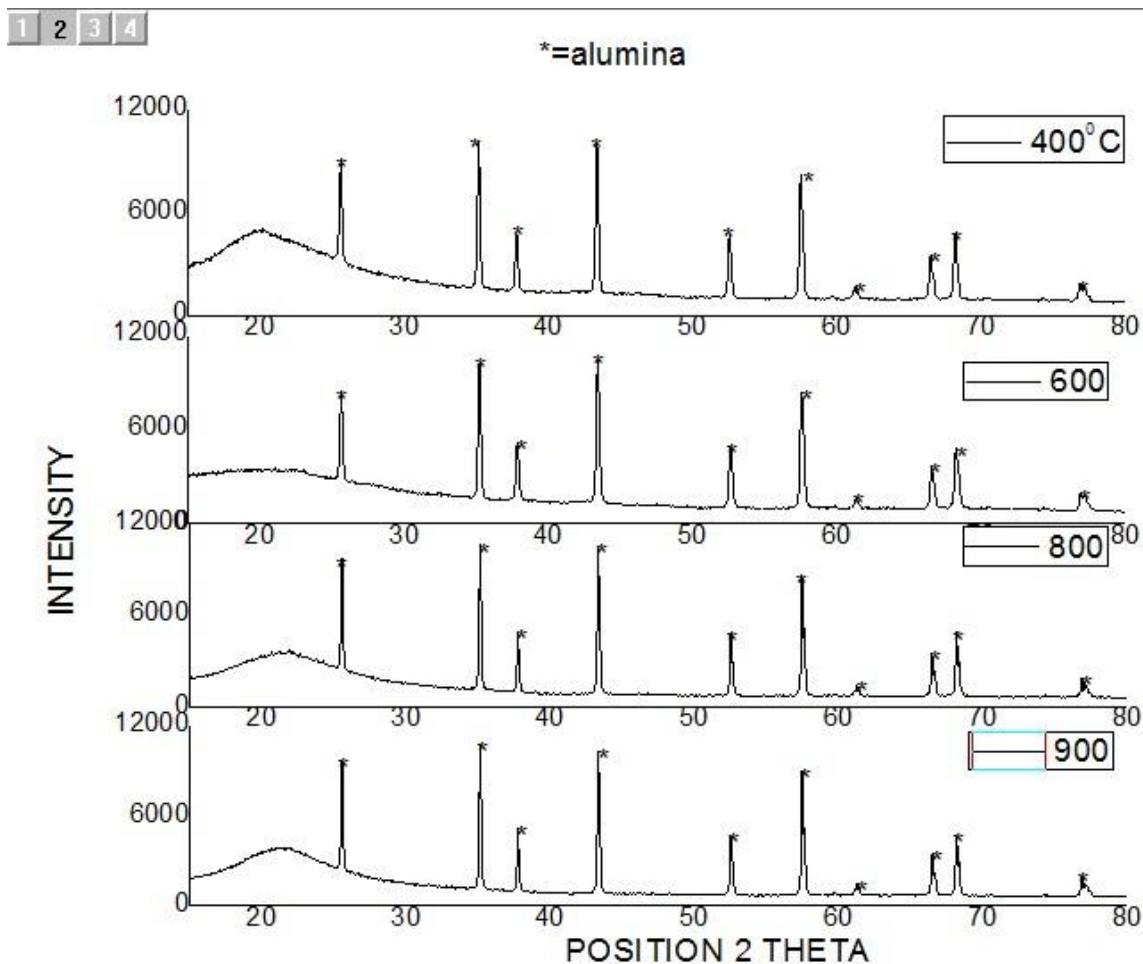This the XRD plot of the raw microcrystalline alumina powder taken as a raw material for batch synthesis.

XRD plot of microcrystalline alumina
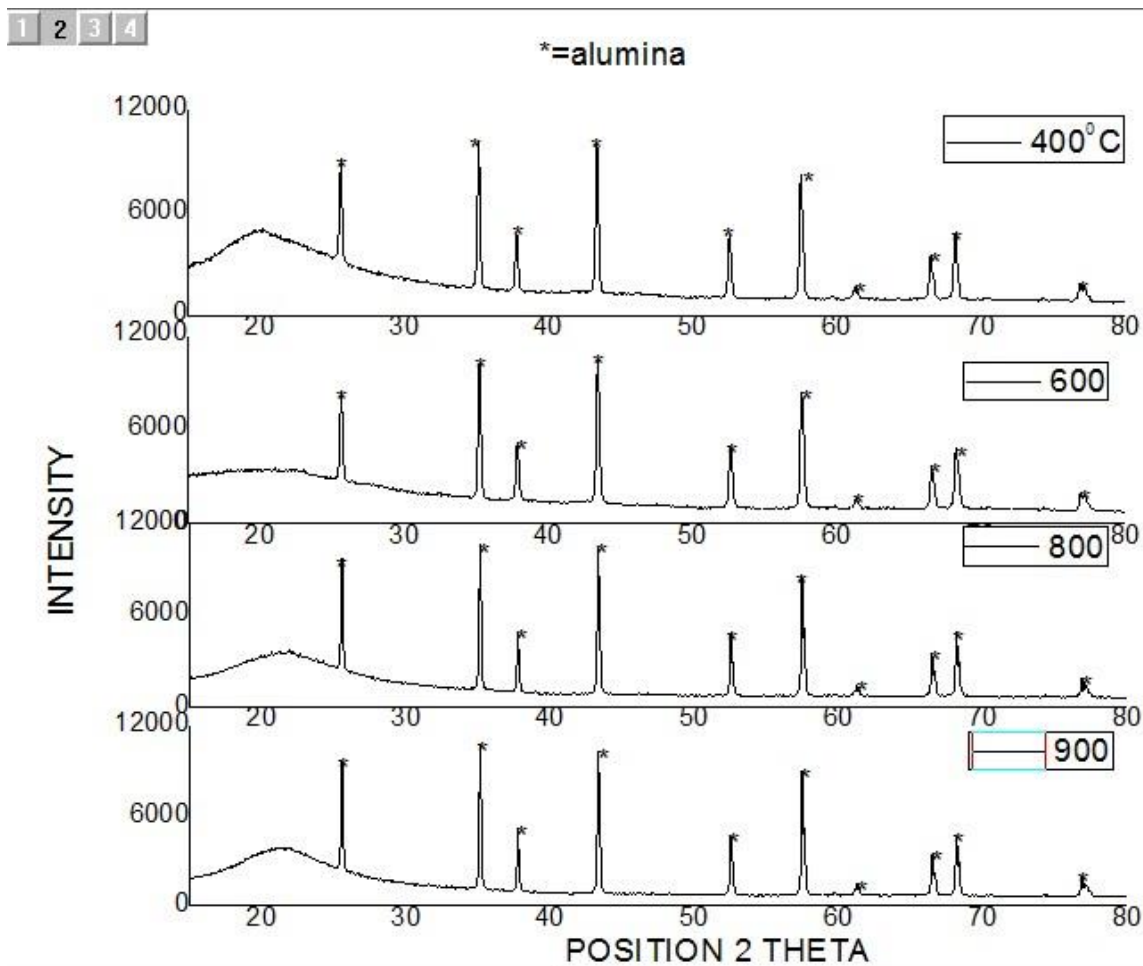
XRD plot of 7:3 powder of all temperatures

According to the XRD Plot obtained, only alumina peaks were obtained and no traces of mullite were found for this composition.

XRD plot of 8:2 powder of all temperatures

According to the XRD Plot obtained, only alumina peaks were obtained and no traces of mullite were found for this composition

XRD plot of 9:1 powder of all temperatures

According to the XRD Plot obtained, only alumina peaks were obtained and no traces of mullite were found for this composition

Crystallite size (D_p) Size using XRD plot

Sample Comp.	Pyro.temp.(^{0}c)	Max.Peak angle	FWHM(rad)	D_p
70-30	400	35.1868	**0.1476**	**172.03**
	500	35.1639	**0.1476**	**171.92**
	600	35.1537	**0.1968**	**128.98**
	800	35.1868	**0.1968**	**128.87**
	900	35.1880	**0.1968**	**128.82**
80-20	400	43.3793	**0.1476**	**132.59**
	500	43.3972	**0.1476**	**132.82**
	600	43.4333	**0.2460**	**105.48**
	800	43.1586	**0.1476**	**131.67**
	900	43.1639	0.1476	131.89
90-10	400	35.0542	0.1476	171.98
	500	35.0141	0.1476	171.57
	600	43.4325	0.1968	132.32
	800	35.1645	0.1476	170.83
	900	35.1662	0.1476	170.94

BET ANALYSIS

Sample ID   7030-600

Description   70(h44)-30(alumina)-600^{0}C

Sample Weight   0.0337 g

MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
1.0533e-01	117.5187	8.015E-01
1.5612e-01	119.8780	1.235E+00
2.0612e-01	121.4181	1.725E+00
2.5847e-01	122.4092	2.278E+00
3.0909e-01	123.1036	2.908E+00

Area = 3.497E+02 m²/g
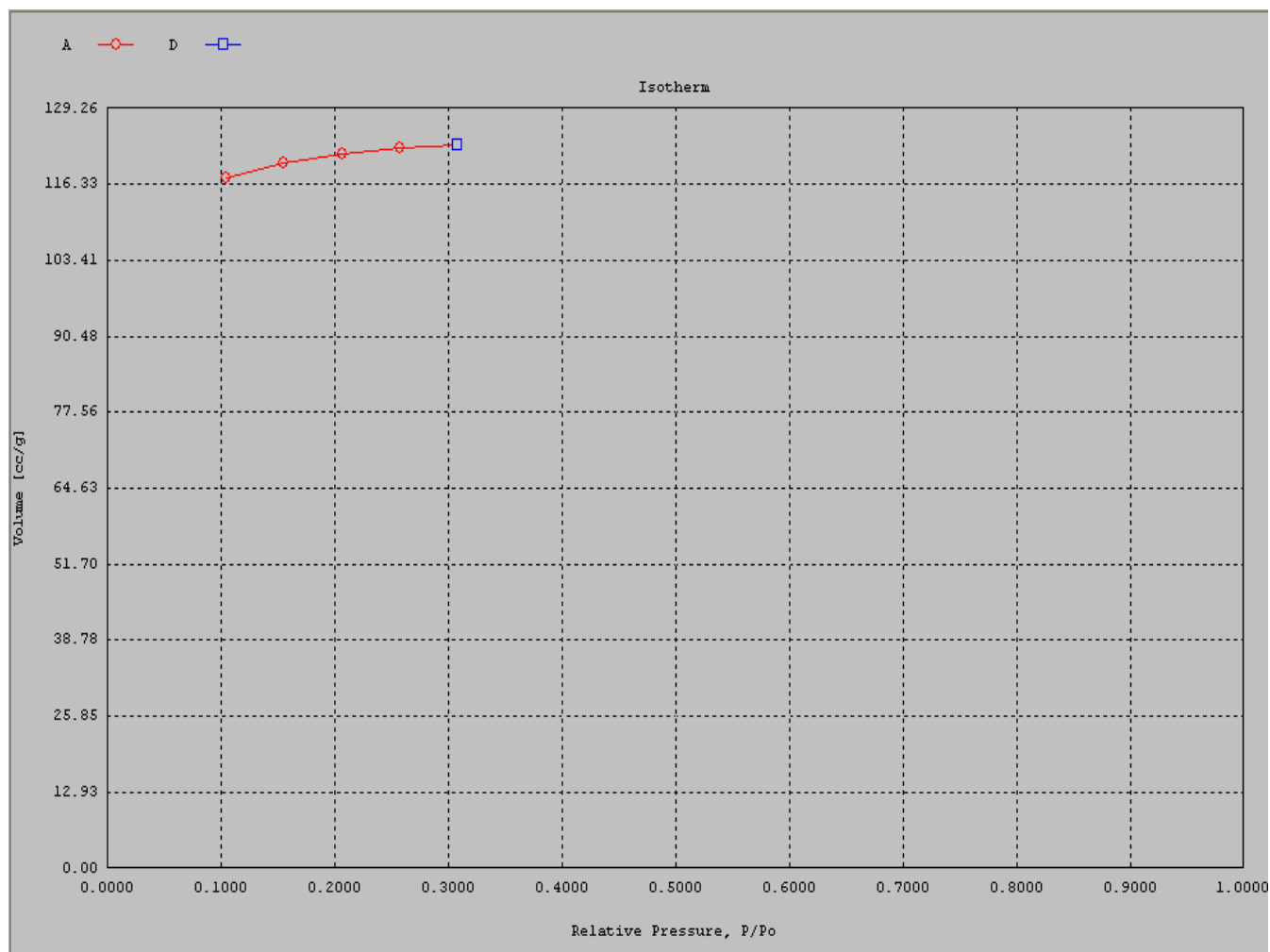
RELATIVE PRESSURE Vs VOLUME

PORE VOLUME

Sample ID   7030600

Description   70(h44)-30(alumina)-600^{0}C

TOTAL PORE VOLUME

**Total pore volume = 1.904E-01 cc/g for**

pores smaller than 26.4 Å (Diameter),

at P/Po = 0.30909

PORE SIZE DISTRIBUTION

Sample ID   703060

BJH ADSORPTION PORE SIZE DISTRIBUTION

| Diameter, Å	Pore Vol [cc/g]	Pore Surf area [m²/g]	Dv(d)	Ds(d))	Dv(log d)	Ds(log d)
17.18	9.632E-03	2.242E+01	3.823E-03	8.902E+00	1.510E-01	3.515E+02
19.71	1.585E-02	3.504E+01	2.452E-03	4.976E+00	1.111E-01	2.255E+02
22.29	1.980E-02	4.214E+01	1.507E-03	2.704E+00	7.723E-02	1.386E+02
25.00	2.259E-02	4.660E+01	9.907E-03	1.592E+00	5.721E-02	9.153E+01
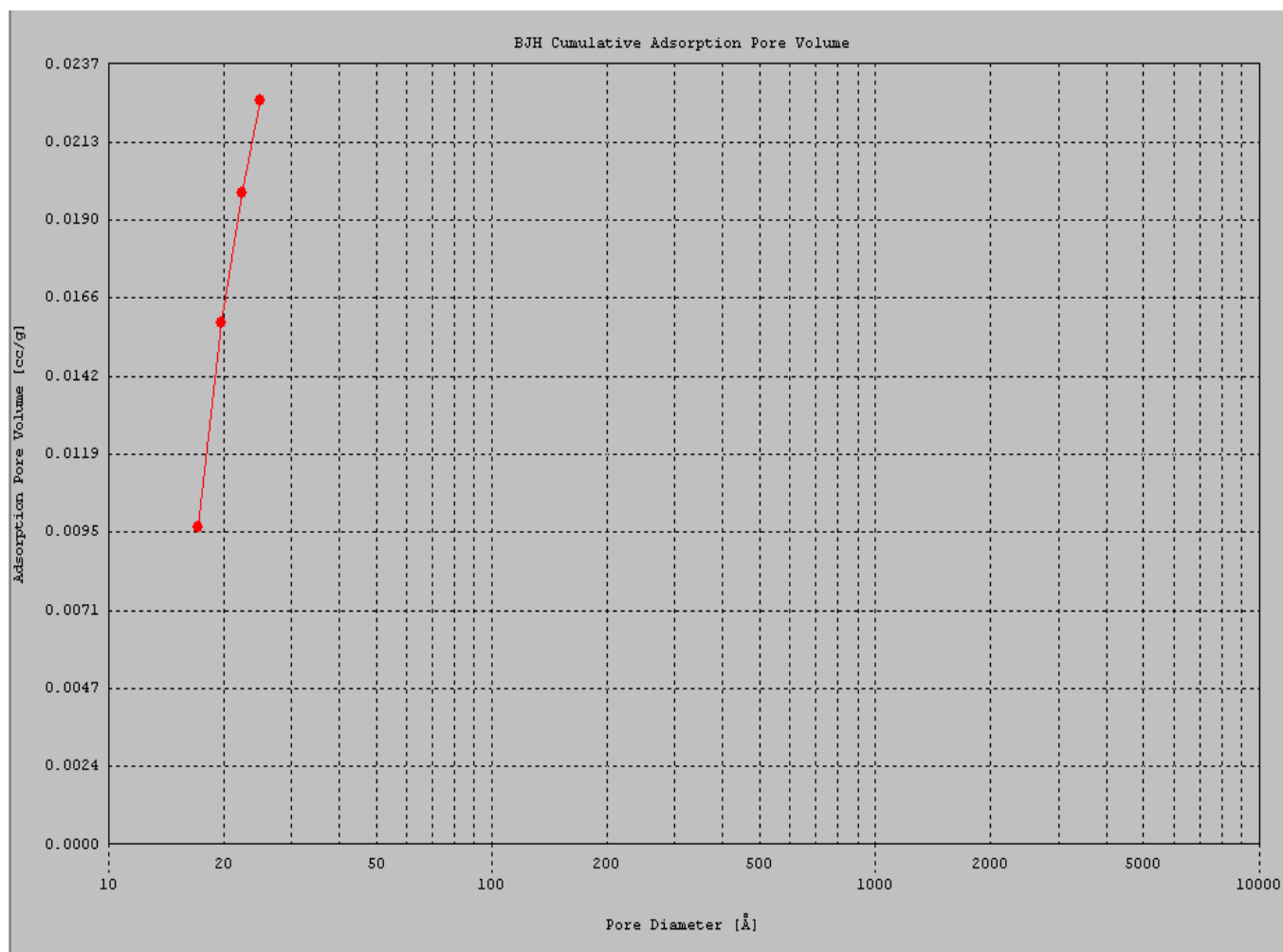
BJH PORE DIAMETER Vs PORE VOLUME

ULTRAVIOLET-VISIBLE SPECTROSCOPY (FOR ABSORPTION EFFICIENCY)

UV-VIS spectroscopy was performed to study the preliminary adsorption properties of these hybrids for toxic ion removal. Thymmol blue ($C_{27}H_{30}O_5S$,mol wt.- 466.60 g)indicator was taken for this purpose. A 100 ppm standard solution and solution of 7030 composition were prepared and UV-VIS Spectroscopy was done(400nm-700nm).Then Beer-lamberts law was used to determine the absorption efficiency.The absorption value of the standard solution was found to be 1.3404. The result obtained were as given below-

Sample composition	pyro.temperature(in ^0C) and shaking time	λmax	Absorption	Efficiency(%)
70-30T	600-30 mins	433 nm	1.1003	22.10
	60 mins	433 nm	1.0530	27.60
	800-30 mins	433 nm	1.0696	25.10
	60 mins	433 nm	1.0620	26.55
	900-30 mins	433 nm	1.0624	26.50
	60 mins	433 nm	1.0250	31.12
PURE ALUMINA	30-60 mins	433nm	1.030	30.48

From the above data,it can be inferred that, the hybrid samples which are pyrolysed at relatively higher temperatures show better ion absorbing capacity.The highest efficiency was obtained for

that of 900^0C pyrolysed-70-30 sample (31.12 %) which is slightly higher than that of pure alumina (30.48).The λ_{max} was obtained at 433 nm.

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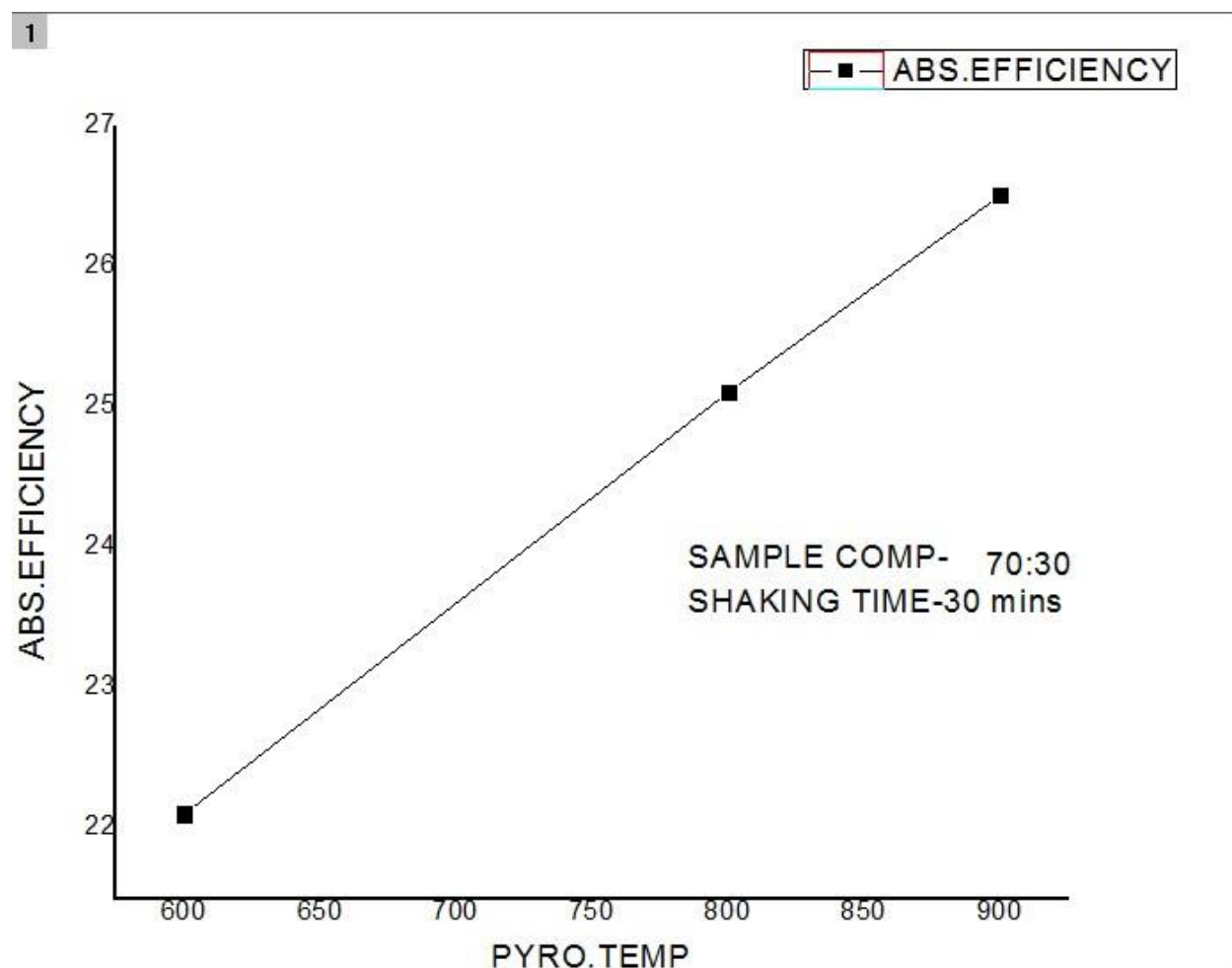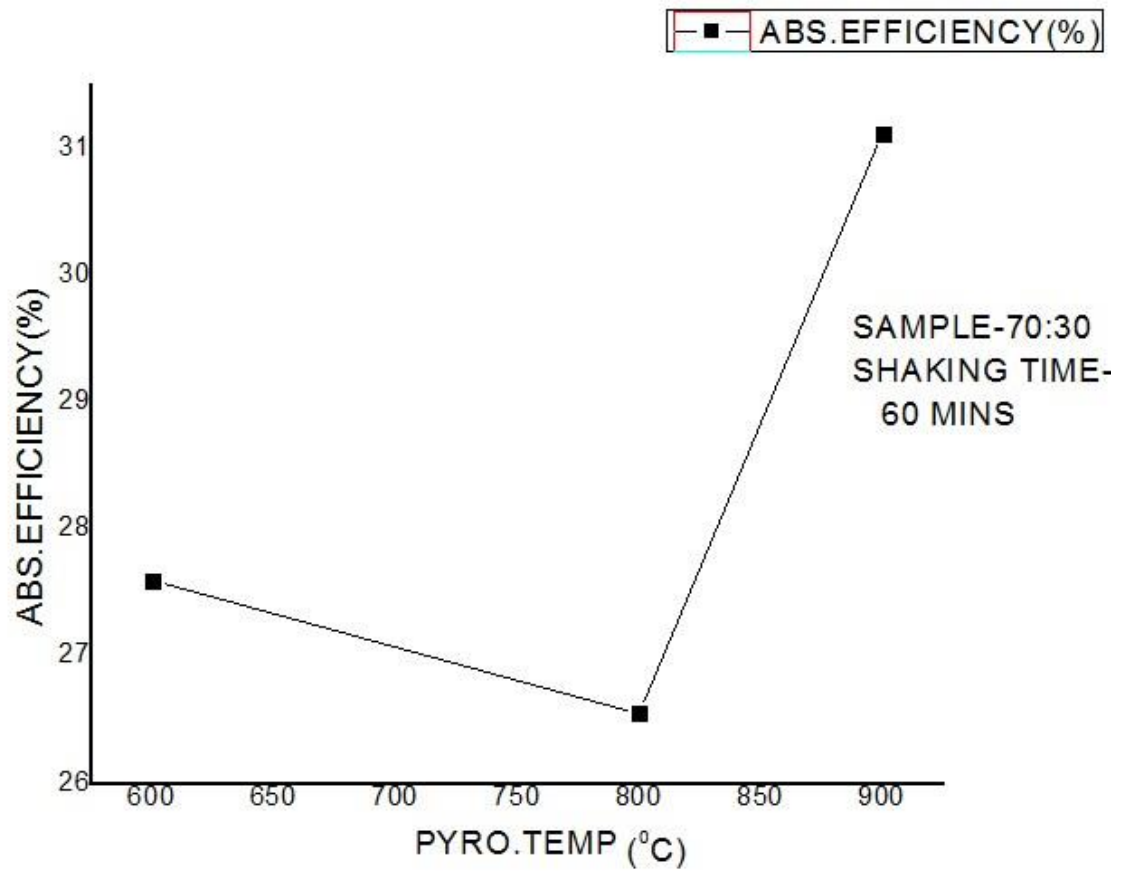
CHAPTER-6
CONCLUSION

From all the above experiments and data we can successfully conclude that-

1. That the hybrids(alumina-silicon oxycarbide) could be prepared from a hard oxide(alumina in this case) and a polymer that can be blended(H-44,Polymethylphenylsilsesquioxane).In this case the H-44 polymer coats the alumina surface.

2. Various ratios(by varying the alumina/H44 cmposition) can be followed to tailor the properties of the hybrid, as was seen from the experiments.

3. The size of the hard oxide (alumina here) can be changed to some other oxide by pyrolysis and blending with the silica polymer, and the size of the particles can also be changed to formulate hybrids of different chemical and physical properties.

4. Although surface area analysis could not be carried out comprehensively on the fabricated samples, one test (7030 pyrolysed at 600^0 C) revealed that 350 m^2/gm surface area can be attained with the use of microcrystalline powders.

5. Degradation of Thymmol blue indicated that the materials can be effective in adsorbing toxic ions. However, we expected the low temperature pyrolyzed samples to be more effective, which was not the case as can be seen from the results. We expect that the hydrophobicity of the powders that were pyrolyzed at a lower temperatures could be the cause.

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5. Kinetic Studies of Mullite Synthesis from Alumina Nanoparticles and a Preceramic Polymer Flavio Griggio, Enrico Bernardo,w and Paolo Colombo* Universita` di Padova, Dipartimento di Ingegneria Meccanica—Settore Materiali, Via Marzolo, 9, 35151 Padova, Italy

G. L. Messing* Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16801.

6. Anran Guo, Martina Roso, Michele Modesti, Jiachen Liu, Paolo Colombo et al,2013.