Isolation and Charcterization of Iron Nanoparticles From Coal Fly Ash From Gandhinagar (Gujarat)Thermal Power Plant (A Mechanical Method of Isolation)

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Abstract:**Coal fly ash is one of the richest sources of iron nanoparticles among waste. Fly ash contains many nanominerals and nanoxides, along with some heavy metals. But iron and silica is present in maximum amount. So, here iron and iron nanoparticles were successfully isolated and characterized, from coal fly ash, collected from one of the thermal power plant, from Gandhinagar. Fly ash is generally a waste by product for thermal power plant. So, it's a novel method to utilize waste for synthesizing nanoparticle. In this study iron nanoparticles was isolated and characterized by TEM, DLS and zeta potential, UV-VIS, PSA (Particle size analyzer).**

Keywords:Fly ash, Class F, Iron nanoparticles, Non Zero valent iron, TEM, UV-VIS, PSA

INTRODUCTION

Most of the thermal power plants in India utilize high-ash bituminous coal for combustion in pulverized fuel fired systems. In India low lime fly ash which is similar to Class F is the prime variety generated. Fly ash is the fine grained powder produced from the mineral matter present in coal, plus a small amount of carbon that remains due to incomplete combustion. Fly ash is the finest of coal ash particles. It is carried through flue gas and collected from the flue gas by means of electrostatic precipitators, bag-houses, or mechanical collection devices such as cyclones.

In India, maximum number of thermal power plant about, 84% are running on coal with 70 billion tonnes of coal reserve, while the remaining ones on gas and oil. [1]. Approximately 112 million of tonnes of fly ash is being generated annually in India by thermal power plants as a byproduct of coal combustion. Fly ash has about 70% of total residue that are generated in coal-fired power plants equipped with electrostatic precipitators or bag filters. Only 10% is utilized while up to 90% is buried in fly ash pond.[**2**]Quality and composition of fly ash depends on the type of coal used, combustion technique, air/fuel ratio and boiler type.

In 100 gm of fly ash there are 10% iron particles, so what about 112 million tonnes of fly ash? For instance,

In 100gm of fly ash– 10 gm iron particles

So, in 112 million tonnes ~ 112 x10^6 kg iron particles, which can be further converted into nanoparticles?

From the above calculation, it is evident that, a huge amount of iron particles could be collected from fly ash which is actually a waste and can add up in a country's total economy. The iron particles obtained from the fly ash can be used as a raw material for a number of iron based reactions. It can be further recycled and purified.

Fly ash is used in agriculture as a fertilizer, herbicide, in civil engineering works i.e. for cement manufacturing, brick making, for making light weight aggregates, as landfill, for road stabilization, for ceramic tiles, used in mines.Among nanomaterials which are present in fly ash, iron oxide (mainly hematite and magnetite) are the main bottom ash products of the oxidation of pyrite, sometimes via intermediate pyrrhotite formation. The burning of coal produces airborne derived nanosized particles of size (typically< 100nm in size).[**3**]

Iron is one the most important element in nature as well as in our life. It is actually an essential element that is required in trace amount for vital functioning of cells, tissue and other living being. The various applications of iron in living beings could be possible due to the variable oxidation state of iron, its ability to co-ordinate to oxygen, nitrogen and sulfur atoms and to bind additional small molecules.Currently they are findingapplications in each and every field of life. Today they are being utilized in clinical diagnosis, sensors catalyst, in environmental remediation**.[4]** Nanosciences is playing an important role in the fabrication of new class of materials.Nanosciences isthe branch of sciences that deal with materials whose sizeranges from 1-100nm.Scientists have reported that Non Zero Valent Iron, NZVI, has much higher reactivity than micro or macro sized due to its small size as well as role as an electron donor.Environmental nanotechnology is believed to play an important role in shaping up of current environmental sciences and engineering. In the environment, iron has an important role as a contaminant mobility, sorption and particle breakdown due to its role as an electron donor, and in its several mineral forms, as a precipitant/sorbent substrate.At nanoscale these iron are sub colloidal in size, and unique molecular and atomic structures, so they possess a distinctive mechanical, magnetic,optical, electronic, catalytic and chemical properties, which decodes their further applications. Thedrastic change at nanoscaleis just because of the two fundamental properties of nanoparticles: **1) high surface area to volume ratio 2) quantum effects**.

Chemical composition of Fly ash:-

Fly ash particles are spherical in shape and size ranges from 0.5 micron -100 micron. It contains mostly silicon dioxide (SiO_2) in two forms crystalline and amorphous (both smooth and rounded), pointed and hazardous. It is heterogeneous in nature, consisting of glassy particles as Quartz, Mullite, & iron oxide.Fly ash also contains certain heavy metals like Ag, As, Be, Boron, Cd, Cr, Co, Pb, Mn, Hg, Mo, Se, Thallium and vanadium.The isolated iron nanoparticles can further be modified for environmental application, remediation etc, biomedical for drug delivery and MRI contrast agents etc.

In this study author has collected fly ash from Gandhinagar, Thermal power plant, isolated iron particles and characterized by various instruments i.e. from TEM, DLS, PSA, UV-VIS, etc.

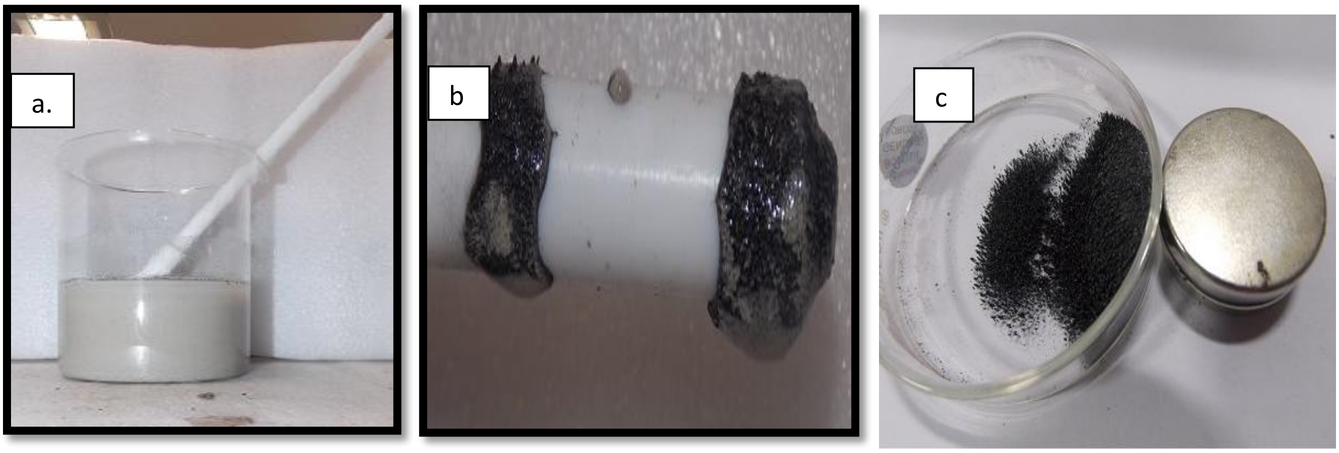
Table1. **Chemical composition of Gandhinagar Fly ash**

S.No	Chemical composition	Percentage %
1.	Silica (SiO_2)	49-67
2.	Alumina(Al_2O_3)	16-29
3.	Iron oxide (Fe_2O_3)	4-10
4.	Magnesium oxide (MgO)	0.2-2
5.	Sulphur (SO_3)	0.1-2
6.	Loss of Ignition	0.5-3.0
7.	Calcium oxide (CaO)	1-4

Materials and methods

Sector, 30 Thermal power plant issituated on the bank of Sabarmati River, Gandhinagar, which is hardly 1km from the university campus.

1. **Sampling**- Fly ash was collected directly from the electrostatic precipitator unit from thermal power plant, Gandhinagar, Sector 30. They were packed in the white transparent polybags.



a) Fly ash slurry b) Iron nanoparticles on magnetic rod c) Iron nanoparticles attracted towards an external magnet

Fig.1. (a-b-c) Process involved in the isolation of iron nanoparticles with a magnetic rod

2. PREPARATION OF 10% FLY ASH AMENDED AQUEOUS SOLUTION

For making 10% fly ash aqueous solution,10 gm of fly ash was weighed and mixed with 1000 ml distilled water. With the help of a magnetic rod, mechanical stirring was done for 10-15 minutes, shown in fig.1a. Iron bearing particles stuck to the magnetic rod while after few minutes of stirring. Those particles were separated out, and collected on a Petri dish. Again with the help of magnetic rod, stirring was done. Again the particles were separated and collected. This process was repeated several times till; a sufficient amount of iron particles was not obtained. The isolated iron bearing particles was washed 2-3 times with distilled water and then twice with acetone. After that they were dried in a hot air oven at 110 ^{0}C for 3-4 hrs. It was weighed on a weighing balance, and noted down how much iron bearing particles were obtained from 100gm of fly ash. Iron bearing particles were stored in a glass vial. And further used for characterization purpose. The remaining solution was filtered through a Whatman filter paper no.42 and the filtrate was collected and used for studying several water based physicochemical parameters.

3. PHYSICOCHEMICAL FEATURES OF FLY ASH AMENDED SOLUTION

Following characteristics were analyzed:-

1.Physical characteristics:The physical characteristics included temperature, conductivity, turbidity, total dissolved (TDS), Total suspended solids(TSS), Total solids, color.
2.Chemical characteristics: The various chemical characteristics included, hardness (magnesium, and calcium and total), alkalinity, hardness, PH, dissolved oxygen(DO), chemical oxygen demand, Biological oxygen demand(BOD), chloride, nitrate and sulphate.

Table.1 Different parameters of water samples

S.No	Parameters	Value	Method
1.	pH	7.09	pH meter
2.	TDS	0.187 mg/L	Multi water parameter analysis
3.	Calcium hardness	0.8	Chemical method
4.	Magnesium hardness	0.2	Chemical method
5.	Sulphate	36.2	Chemical method
6.	Chloride	12.0132	Chemical method
7.	Dissolved oxygen (DO)	18.03 g/L	Chemical method
8.	TOC, Total organic carbon	21.71mg/l	TOC analyzer (Analytikjena) multi N/C 3100
9.	IC, Inorganic Carbon	8.03mg/l	TOC analyzer (Analytikjena) multi N/C 3100
10.	TC, Total carbon	29.75 mg/ml	TOC analyzer (Analytikjena) multi N/C 3100

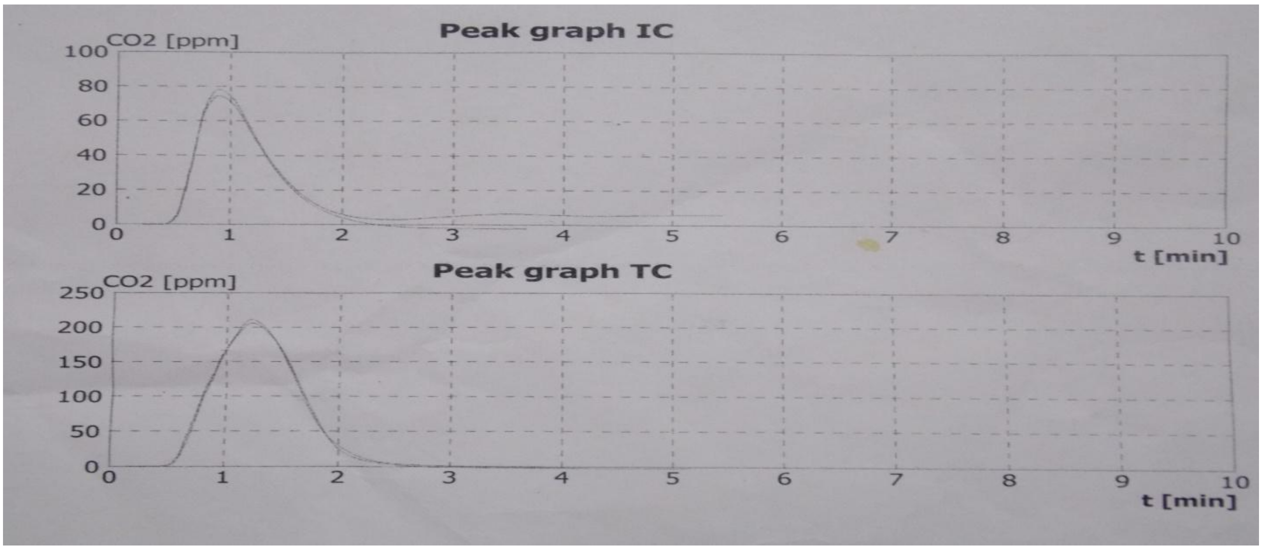


Fig. 2.Graphs showing peaks of Inorganic carbon and total carbon, by TOC analyzer

Carbon is one of the main constituent of coal and due to this reason only TOC analyzer is showing higher value of total carbon .i.e 29.75mg/ml. Total carbon, includes both the organic and inorganic one present in the coal. During the burning of coal, some of the carbons may be organic or inorganic are incompletely burned. So, there is higher value of organic carbon from fly ash i.e. 21.71mg/l.

4. CHARACTERIZATION OF ISOLATED IRON NANOPARTICLES

Sample was characterized with the TEM for its size determination. It was also characterized with PSA, and DLS, SEM, and UV –VIS spectrophotometry.

5. TEM – FOR SIZE AND MORPHOLOGICAL STUDY

The size of the iron particles was determined by the TEM (TECHNAI 200 kv) [Fei, electron optics] at different measurement scale.The sample was prepared in organic solvent, toluene and then, loaded on a copper grid for TEM analysis. The iron nanoparticles were of generally two sizes; one of **7.82nm**, while other was of **33.79** nm. The sample was observed at 29,000X magnification with an accelerating voltage of 20 kV.(**Fig.2.a,b**).It has iron nanoparticles of various shapes i.e. spherical, cuboidal, rhombus and cylindrical. The smallest particle was of**7.82** nm and spherical particle was of **33.79** nm.

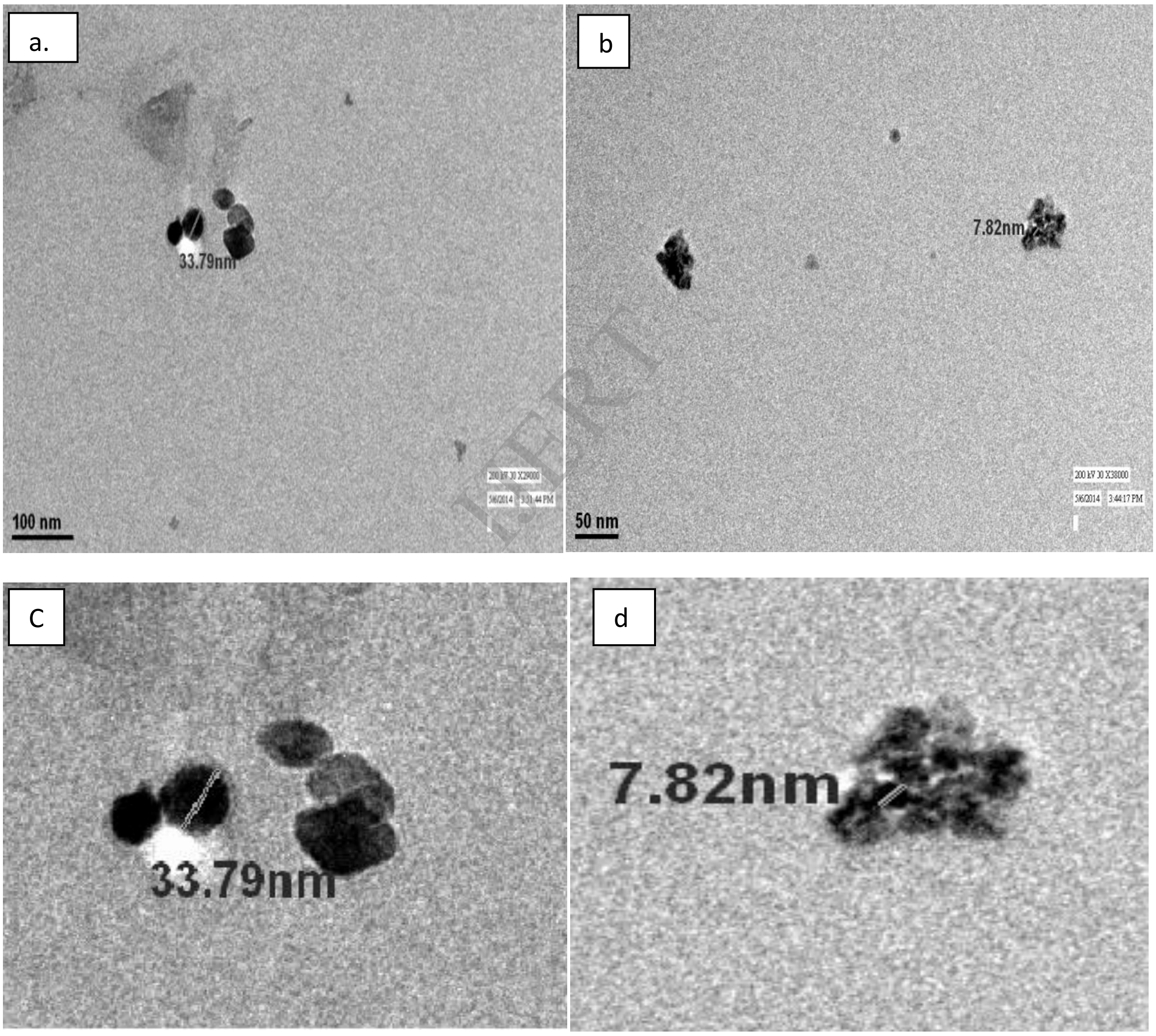


Figure.3. TEM images of Iron nanoparticles-from fly ash

a) At 100nm scale, b) at 50 nm scale c) magnified image of iron nanoparticle at 100nm, d) magnified image at 50 nm scale.

a. DLS and zeta potential

It measures the size of particle on the basis of fluctuations in scattered light intensity with time. These fluctuations are due to therandom Brownian motion of the nanoparticles. The statistical behavior, of these fluctuations in scattered intensity is directly related to the diffusion of the particles. In comparision to larger particles smaller particles diffuses more rapidly, this provides relation between particle sizes to measured fluctuations in light scattering intensity. The Zeta potential is mostly used as an indicator of dispersion stability. Larger the zeta potential value of an electrostatically stabilized suspension, higher will be its stability.

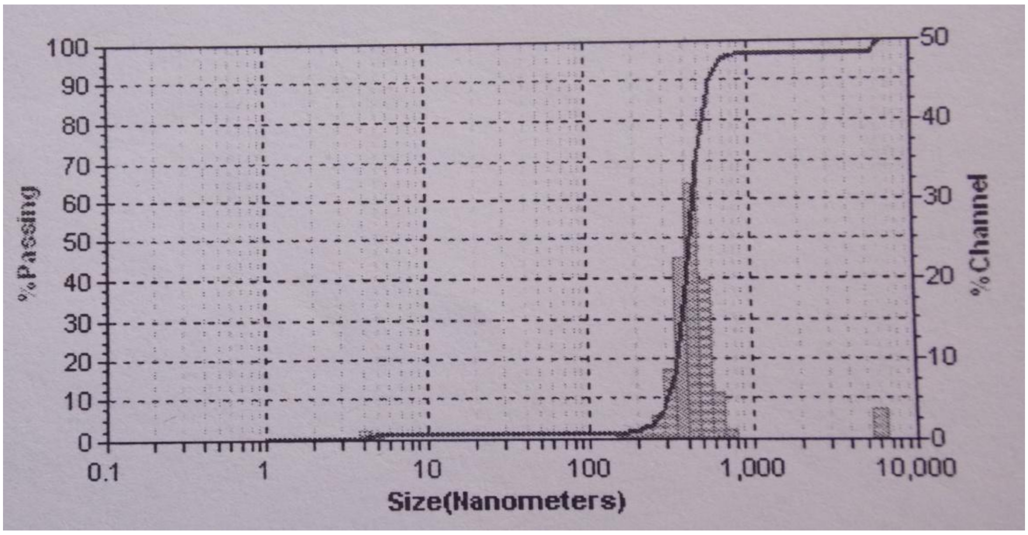


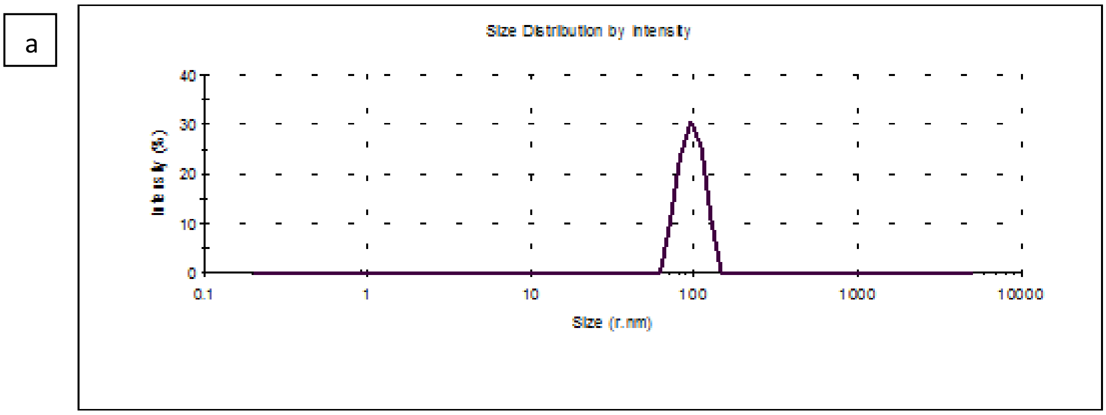
Fig.4 Zeta potential of Fly ash isolated iron nanoparticles

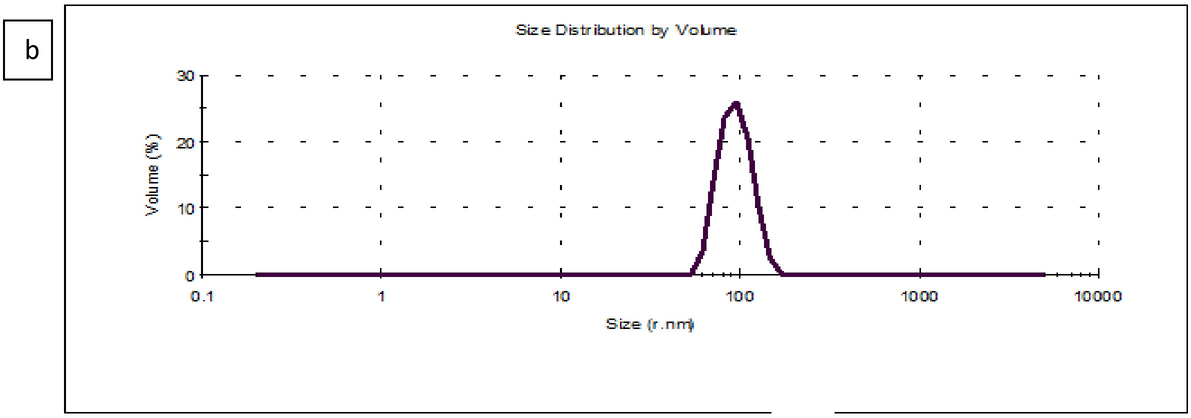
From the fig.3 it is clear that around 60% iron nanoparticles are above 600 nm in size. The mean is coming at 650 nm. It is a heterogeneous in nature as sample has iron nanoparticles of nanoparticles larger than 600nm and also lesser than 600nm.But DLS, don't provide the actual size, as they provide the hydrodynamic radius of the particle.

b. Particle Size Analyzer

Particle Size Analyzer is used for determining the size range, and or the average, or mean size of the particles in a powder or a liquid sample.They use methods such as light scattering, sedimentation, laser diffraction etc to calculate particle sizes. Particle size analyzers can measure the sizes of many particles in a sample very quickly and can provided data on particle size distributions, which is of value to a great many industries.

Particle size was measured, along with distribution of nanoparticles by number, volume and intensity wise with Malvern ZetasizerNanoseries, Nano-S90.The Z-average (r.nm) obtained was 171.9, PDI- 0.538 and the peak was obtained at 87.23 (r. nm). The refractive index of the sample was found 1.52, absorption was 0.100 while viscosity of the dispersion medium was 0.8872. The sample was analyzed at 24.9^{O}C.The distribution of iron nanoparticle is shown in all the three forms in the Fig.**3**(a,b,c)





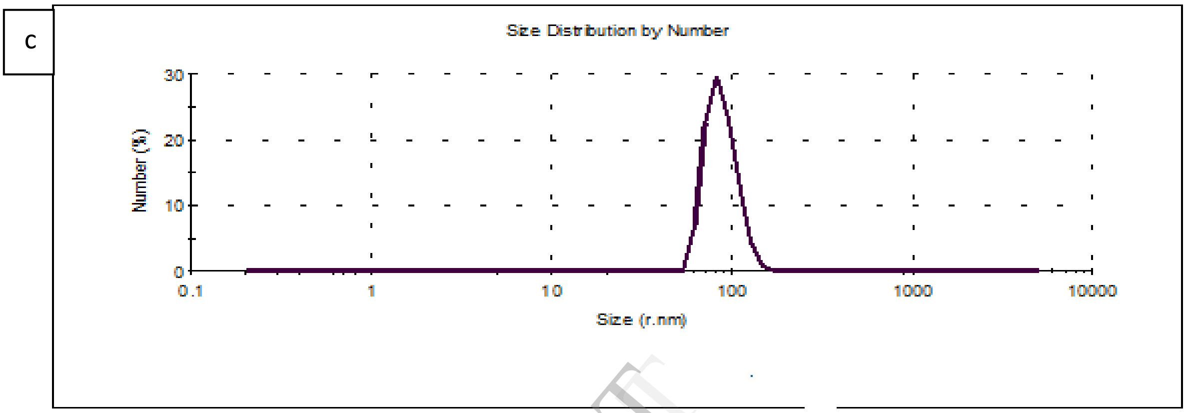


Fig.4.a) Showing Intensity distribution of iron nanoparticles by **b)**Volume distribution and**c**) by Number wise distribution

c. UV-Vis Spectroscopy

It is one of the most universally accepted spectroscopy technique.(UV-VIS) refers to absorption spectroscopy in the UV-Visible spectral region. Here it means that it absorbs light in the visible region and adjacent (near – UV and near -infrared) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.It utilizes the absorption of electromagnetic radiation from ultraviolet to visible. The change in the UV part of the spectrum is due to charge transfer (CT) bands between a surface metal cation and the functional ligand.[5] The maximum absorbance was seen at 200 nm wavelength, 2.79. For Fe^{2+} ions the absorbance spectra is at 200-220nm.

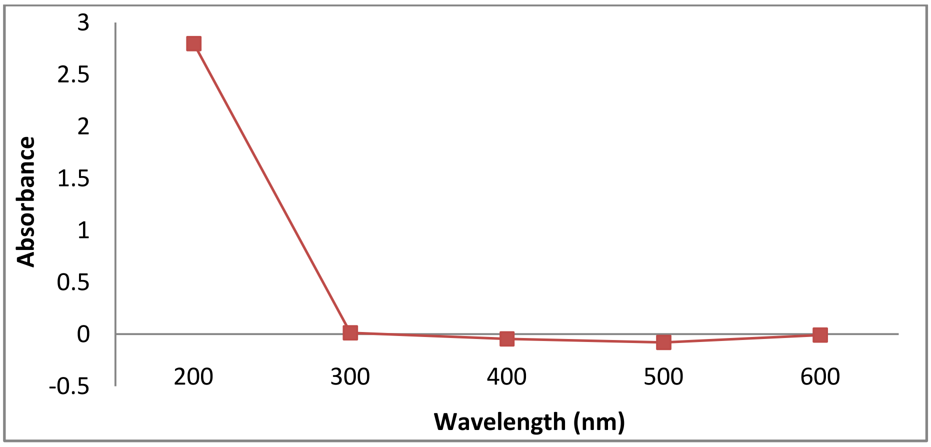


Fig.5 UV-VIS spectra of iron nanoparticles

6. CONCLUSIONS

The present study demonstrated the isolation and synthesis of iron nanoparticles from Fly ash, from one of the thermal power plant of Gandhinagar.It's isolation was very easy, done with the help of a magnetic rod. The isolated iron nanoparticles were characterized with TEM, UV-VIS, DLS, and PSA. Through Tem it was possible to measures the size and shape of different iron nanoparticles present in the sample. While with UV-VIS,it was possible to reveal the presence of iron and associated molecules with that. With PSA iron nanoparticle, volume and number distribution pattern was studied. These iron nanoparticles could be used as a raw material for many materials, for environmental nanotechnology and for biomedical purposes.

7. ACKNOWLEDGEMENT

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8. REFERENCES

1. Chandra A., Chandra H. Impact of Indian and imported coal on Indian thermal Power Plants. J. Sci. Ind.Res. 63, 156, 2004
2. S. Sharma, Fulekar et al., 2009, Fly ash dynamics in soil water systems, Critical reviews in Environmental control, volume 19, issue 3, 1989
3. Luis F.O. SilvaM, Katia M. da Boit," Nanominerals and nanoparticles in feed coal and bottom ash: implications for human health effects" Environ Monit Assess (2011) 174:187–197
4. Kyoungja Woo, et al.," Easy Synthesis and Magnetic Properties of Iron Oxide Nanoparticles", Chem. Mater. 2004, 16, 2814-2818.
5. Madhavi, T.N. Prasad, GajulapalleMadhavi,"Synthesis and characterization of iron based micro and nanoparticles", International Journal of Nanomaterials and Biostructures 2013;3(2):31-34