



Study on the Nature Properties of Fenugreek (*Trigonella foenum-graecum*) at Nanoscale

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Abstract

In this study the Fenugreek seeds are converted to nanoscale and tested for dye degradation, and additionally its thermal withstand range is founded. The size of the particle is confirmed in nanorange with the help of the particle size analyser, and its capacity of dye absorption is analysed by the results of ultraviolet-visible spectroscopy taken at different interval time periods, and the thermal withstand range of fenugreek nanoparticles is measured using thermogravimetric analyser.

Keywords: Mucilaginous fiber, Galactomannan, Thermogravimetric Analyzer (TGA).

1.Introduction:

At present the nanotechnology provides various kind of nanoparticles like ZNO, Silver, TiO₂ etc, for dye degradation but synthesizing these kind nanoparticles requires specific types of precursors and trained lab technician to both synthesize and handle the nanoparticles safely and moreover it requires the external radiation to stimulate the reaction.To overcome or to avoid the use of external radiation for dye degradation this fenugreek nanoparticles are used. Along with dye absorption studies, the thermal withstand range of fenugreek nanoparticles is founded.

The reason for converting fenugreek seeds to nanoscale is that nanotechnology has greater advantage over its “Larger surface area to its volume ratio” so when fenugreek seeds are in Nanoscale a large amount of fenugreek atoms is exposed to the work environment, which makes the Mucilaginous fibre present inside fenugreek nanoparticles to dissolve in water and forms a polysaccharides chain named as galactomannan, At the time of the change from Fiber to Galactomannan certain dye molecules are attached on the polysaccharides chain and settled down at the bottom.

2. Preparation of fenugreek nanoparticles:

The fenugreek seeds are washed with double distilled water in order to remove all the unwanted dust particles which is stucked on the surface of the fenugreek seeds, the washed seeds are taken in pure cotton white cloth and placed under sunlight until the seeds gets dried, these seeds are then transferred to domestic mixer for grinding purpose. The seeds are grinded until a fine powder formation is achieved. These fine powders of 20 grams are separated from domestic mixer and ball milled for 3 hours and the obtained ball milled particles are collected as fenugreek nanoparticles, and this research work is carried out with these 20 grams of fenugreek nanoparticles.

3. Results and Discussion

3.1 Particle Size Analyser

To prove the particles are in nanoscale, the 3 hours ball milled fenugreek particles are analysed for its size distribution range with the help of particle size analyser& the results are shown in Figure 1.

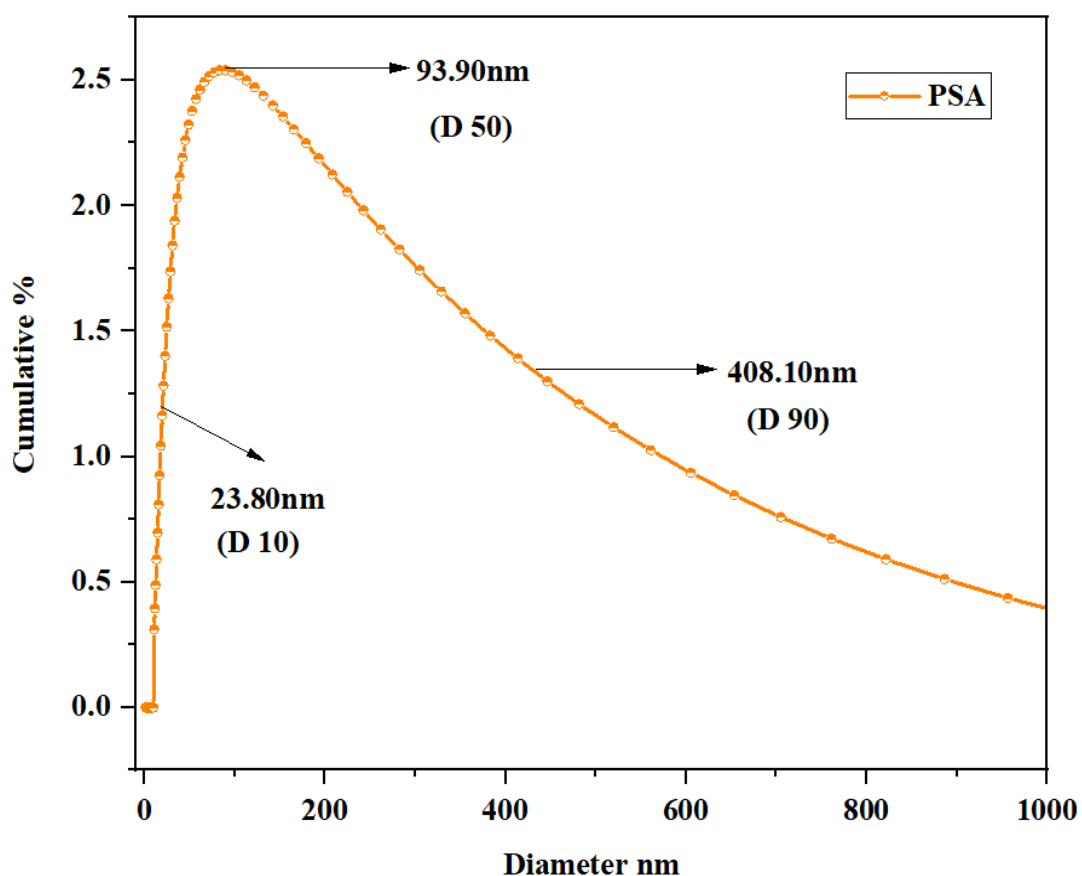


Figure 1 - SIZE OF FENUGREEK NANOPARTICLES

Sl.No	Particle size	Distribution percentage
1	408.10nm	90% at D ₉₀
2	93.90nm	50% at D ₅₀
3	23.80nm	10% at D ₁₀

Table 1 – SIZE OF PARTICLES WITH PERCENTAGE OF DISTRIBUTION

The D₁₀ indicates that 10% of the Fenugreek seeds are in size of 23.80nm, the D₅₀ indicates that 50% of the seeds are in the size of 93.90nm and the D₉₀ indicates that 90% of the seeds are in the size of 408.10nm. The results prove that 60% (D₁₀+D₅₀) of fenugreek seeds are in nanoscale.

3.2 X-RAY DIFFRACTION ANALYSIS:

The study for fenugreek nanoparticles is done for the first time. A Xray of 1.5406 Å is passed over fenugreek nanoparticles and the obtained XRD pattern is given in the below graph.

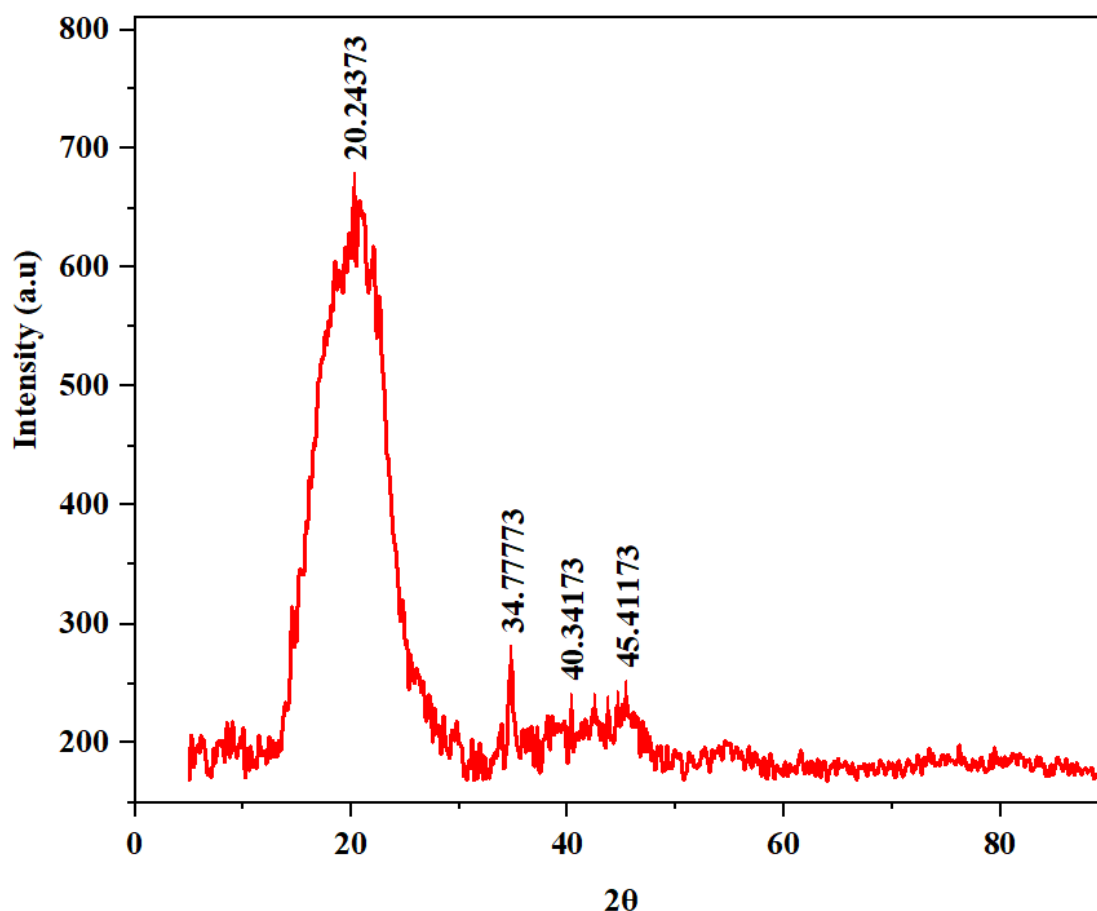


Figure 2- XRAY DIFFRACTION OF FENUGREEK NANOPARTICLES

The results shows that there is one major peak at 20 degrees with an intensity of 667(a.u) the other three are minor peaks with low intensity. To identify crystallinity percentage of fenugreek nanoparticles the percentage of crystallinity calculation is done, which includes the formula

$$\text{Crystallinity percentage} = \frac{\text{Area of crystalline peaks} * 100}{\text{Total area}}$$

The area of crystalline peak is 7380.56 and the total area is around 17761.38, these values are applied on the above formula which gives a crystallinity percentage of around 41.55%, which proves that fenugreek nanoparticles are Semi-crystalline in nature.

3.3 FTIR (FOURIER TRANSFORM INFRARED SPECTROSCOPY)

The FTIR analysis for fenugreek nanoparticles is carried out using (FTIR; Spectrum100; PerkinElmer, USA).

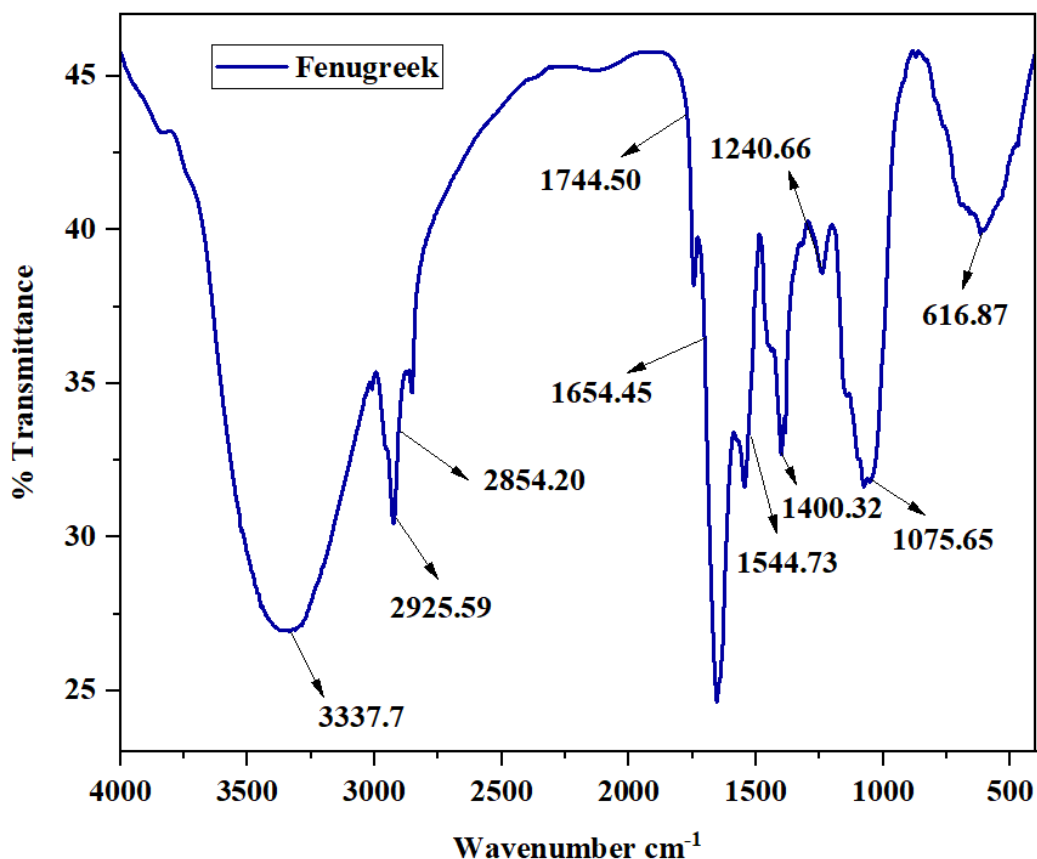


Figure 3- FTIR PEAKS OF FENUGREEK NANOPARTICLES

The Vibrational Data of Fenugreek Nanoparticles is Characterised in two forms, one is the functional group of wavenumbers between 1500 – 4000 cm^{-1} and the other one is the fingerprint regions which is in the wavenumber between 400 – 1500 cm^{-1} the below table shows the wavenumber of the obtained peaks with the transmittance percentage.

Functional Group	Fingerprint Region
3337.71 cm^{-1} , 26.95% T – (O-H Stretching)	1400.32 cm^{-1} , 32.70% T – (C – F Stretching)
2925.59 cm^{-1} , 30.44% T – (C-H Stretching)	1240.66 cm^{-1} , 35.60% T – (C – N Stretching)
2854.20 cm^{-1} , 34.69% T – (C-H Stretching)	1075.63 cm^{-1} , 31.64% T – (C – O Stretching)
1744.50 cm^{-1} , 38.19% T – (C=O Stretching)	616.87 cm^{-1} , 39.85% T – (C – Br Stretching)

Table 2 - FTIR PEAKS WITH TRANSMITTANCE PERCENTAGE

The Functional group peak of 3337.71 cm^{-1} is very strong and broad and the compound class present in this peak is Alcohol [12], the 2925.59 cm^{-1} consists of C – H as symmetric strong vibration, The 2854.20 cm^{-1} peak is symmetric C – H strong [13], the final peak in the Functional group is 1744 cm^{-1} , the peaks consist of C – O (ester carbonyl group)

The Fingerprint region in the peak of 616.87 cm^{-1} is strong and the compound present in this peak are halo compounds, the second peak is 1075.63 cm^{-1} consists of starch OH and cellulose, the third peak obtained in the fingerprint region is 1240.66 cm^{-1} , NH bending (amide III), the final peak in the Fingerprint region is 1400.32 cm^{-1} CH₂ waging.

3.4 UV VISIBLE SPECTROSCOPY ANALYSIS

The result of UV Visible analysis is shown in the Figure 4. The atoms present in fenugreek nanoparticles are founded to be excited at 388nm with a absorbance of 3.92(a.u) which shows that they have the excitation range in visible region.

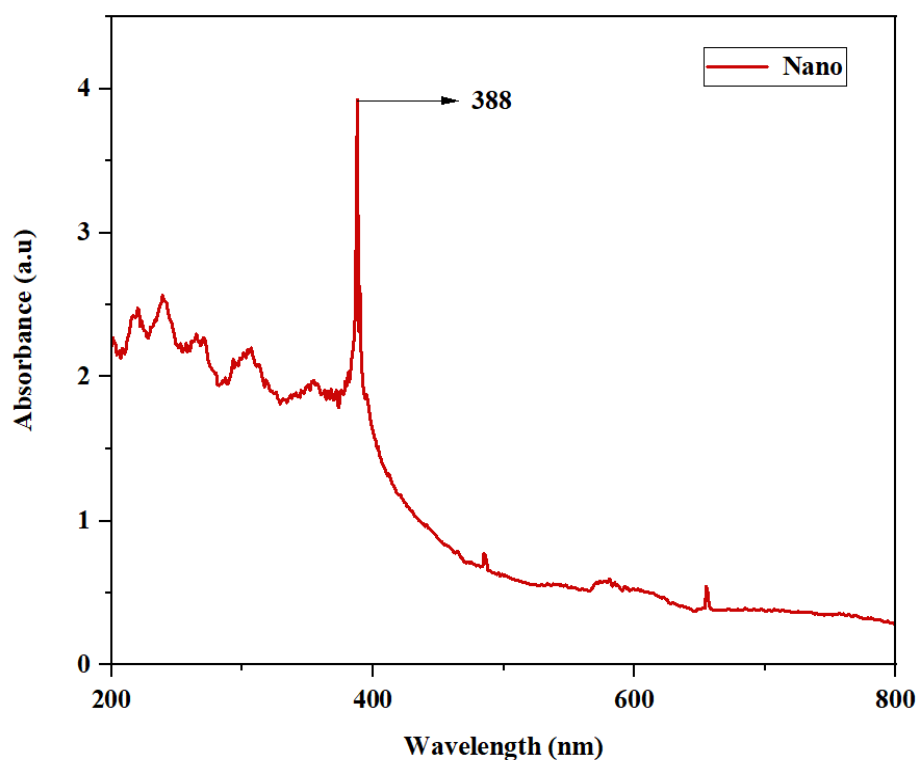


Figure 4 - UV PEAK OF FENUGREEK NANOPARTICLES

3.5 Photoluminescence study

The excitation range of atoms present in fenugreek nanoparticles is identified as 388nm in UV-visible spectroscopy, now its fluorescence emission range is identified in this study, the result of photoluminescence study is shown in the figure 5. The emission range of fenugreek nanoparticles is around 775nm with an absorbance of 59(a.u).

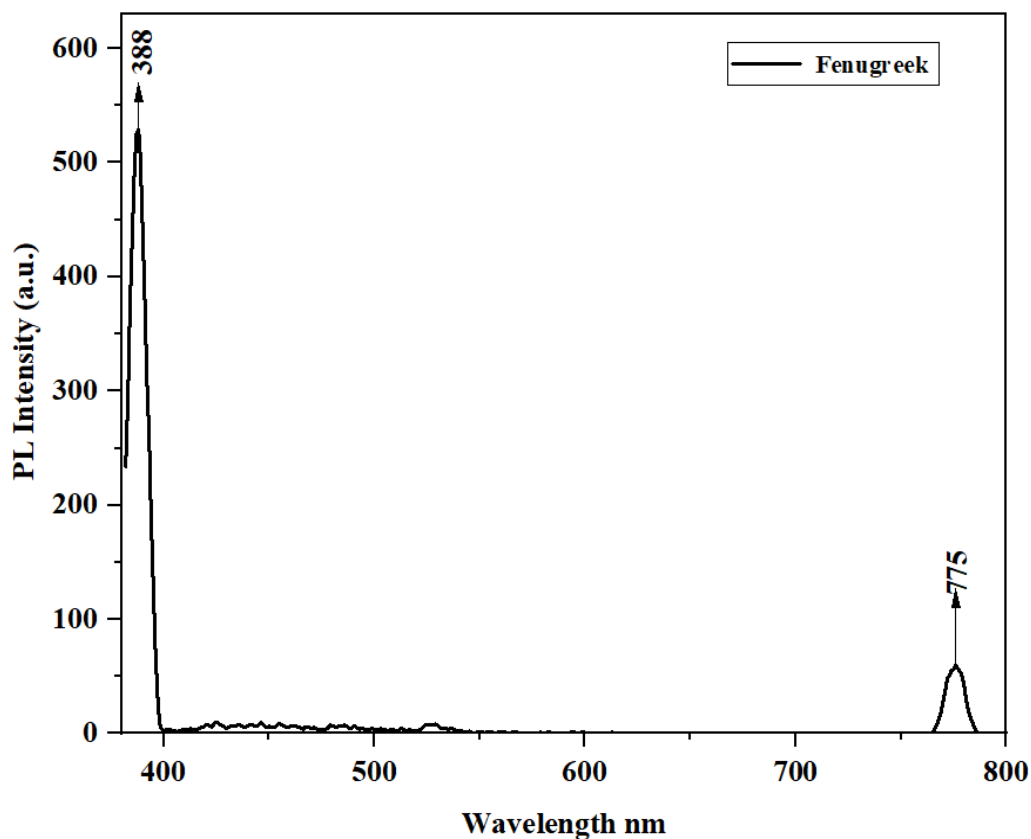


Figure 5 - PHOTOLUMINESCENCE PEAKS OF FENUGREEK NANOPARTICLES

3.6 Study over Dye:

The dye absorption study of fenugreek nanoparticles is carried out with one Cationic and one Anionic dye [15-18]

3.6.1 Study over Methylene Blue

Methylene blue is a cationic dye. A concentration of 100 μ l of dye is mixed with 40 ml of double distilled water, the absorbance of 1.0 (a.u) with excitation range of 664nm is obtained for the taken dye solution. To carry out the study, fenugreek nanoparticles of weight 50 mg are taken and mixed with 40 ml of dye solution and the change in the absorbance is tested at every 30 minutes, the obtained result is given in the below graph.

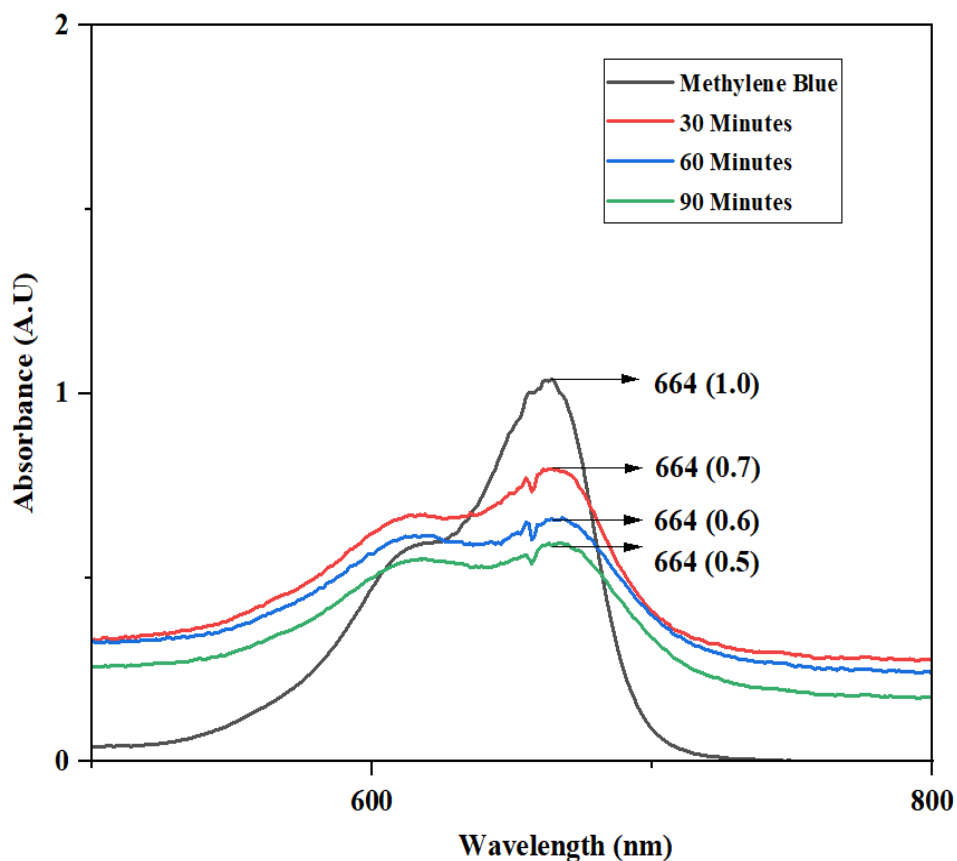


Figure 6 - UV ABSORBANCE OF METHYLENE BLUE

Figure 6 shows that at each 30 minutes there is a decrease in the value of absorbance this is due to the reaction between the mucilaginous fibre present inside the nanoparticles and the dye solution, during the reaction fibre dissolves in dye solution and gives rise to galactomannan a polysaccharides chain in this chain certain methylene blue dye molecules are attached and settled down at the bottom of the beaker, after 90 minutes there is no further decrease in the value of absorbance, this proves that 50mg of nanoparticle are capable of degrading dye up to 90 minutes. Figure 7 shows dye degradation percentage of methylene blue against fenugreek nanoparticles.

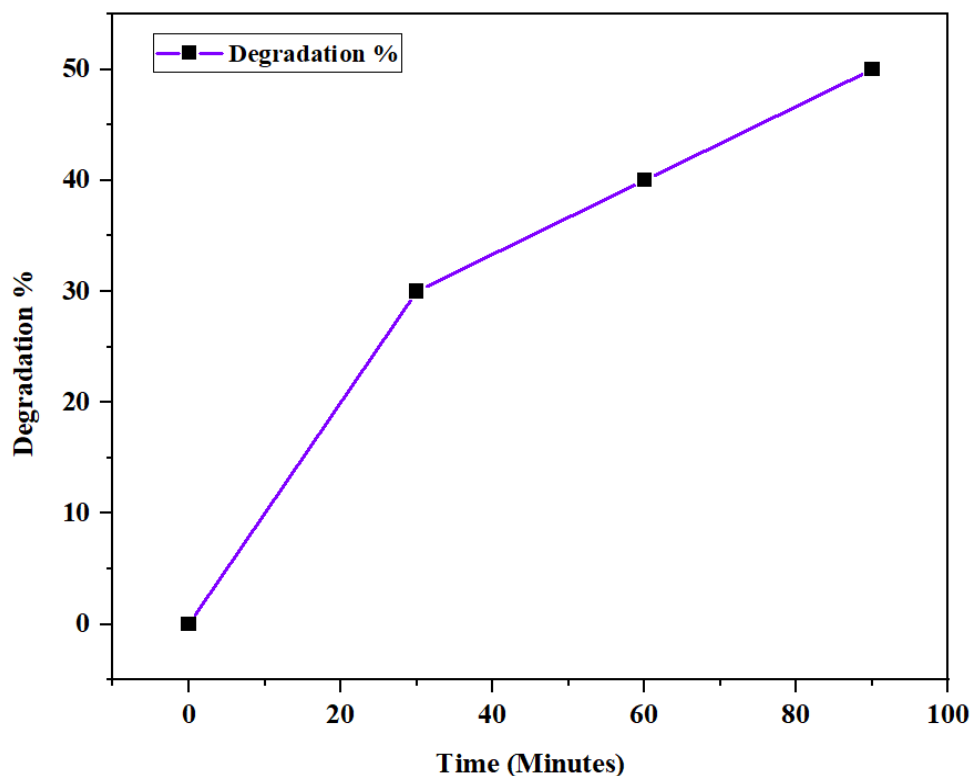


Figure 7- DEGRADATION % OF METHYLENE BLUE

The percentage of dye degradation is calculated with the below formula:

$$D (\%) = (A_0 - A_t) / (A_0) \times 100$$

The A_0 is initial value of UV absorbance which had been taken for dye solution before addition of fenugreek nanoparticles and A_t is the value of UV absorbance after addition of fenugreek nanoparticles which is taken at three interval periods, by using the formula and obtained absorbance value, the percentage of methylene blue dye degradation is founded to be 50%, after 90 minutes of reaction with 50 mg of fenugreek nanoparticles.

3.6.2 Study over Eosin solution

Eosin solution is an anionic dye. A concentration 200 μ l of eosin dye is mixed with 40 ml of double distilled water and the UV excitation peak is founded at 517nm with an absorbance of 1.3 (a.u) is obtained for the taken dye solution. To carry out the degradation study of Eosin solution, fenugreek nanoparticles of weight 50 mg are taken and mixed with the above eosin dye solution and the obtained result at various time period is given in the below figure 8.

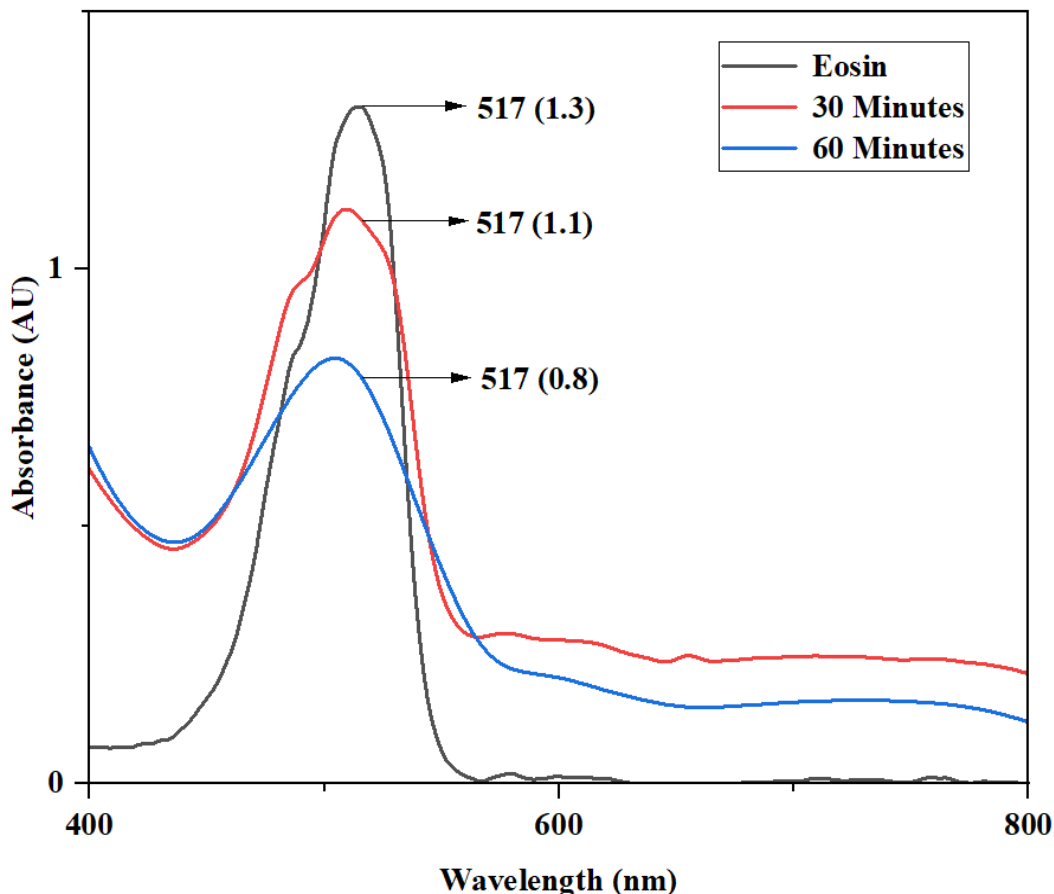


Figure 8- UV ABSORBANCE OF EOSIN SOLUTION

After the fenugreek nanoparticles is mixed with the eosin dye solution there is a decrease in the value of absorbance this is due to the reaction between the mucilaginous fibre present inside the nanoparticles and the eosin dye solution, during the reaction fibre dissolves in eosin dye solution and gives rises to galactomannan a polysaccharides chain during the formation of chain certain eosin dye molecules are attached and settled down at the bottom of the beaker, and after 60 minutes there is no further decrease in the value of absorbance, Hence 50mg of nanoparticle are capable of degrading eosin dye solution of 40ml only up to 60 minutes. Figure 8 shows dye degradation percentage of eosin dye solution against fenugreek nanoparticles.

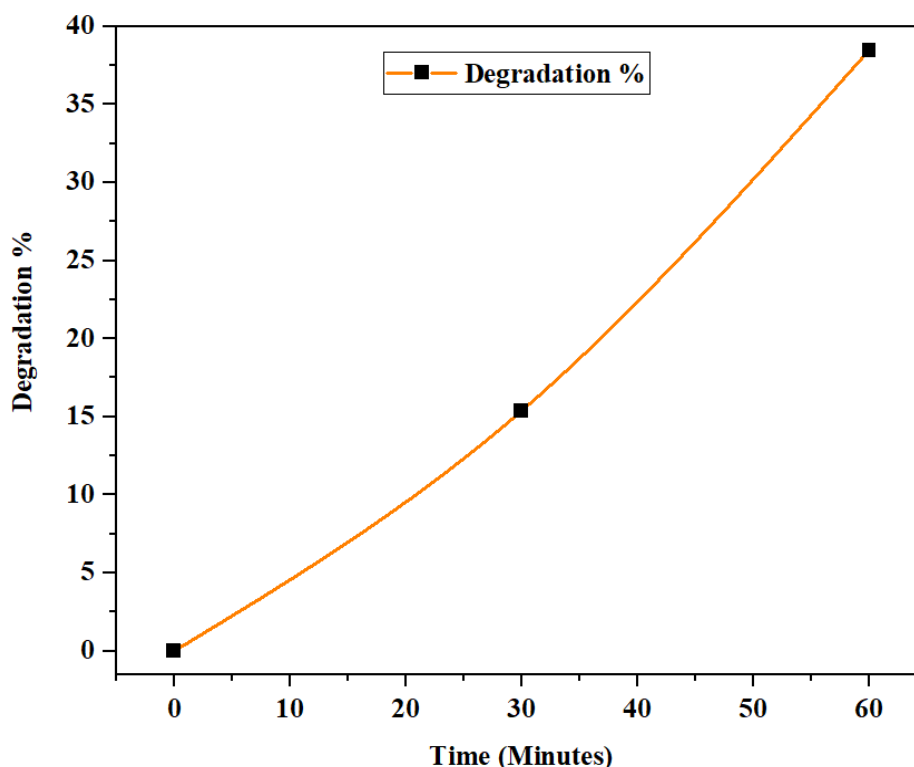


Figure 9- DEGRADATION % OF EOSIN SOLUTION

The percentage of dye degradation is calculated with the below formula:

$$D (\%) = (A_0 - A_t) / (A_0) \times 100$$

The A_0 is the initial value UV absorbance of eosin dye solution before addition fenugreek nanoparticles and A_t is value of UV absorbance after addition of fenugreek nanoparticles and it is taken at two interval periods, using the formula and obtained value of absorbances, the eosin solution degradation is founded to be 38% after the reaction time of 60 minutes with 50 mg of fenugreek nanoparticles.

Sl.NO	Type of dye	Name of the dye	Degradation %	Volume of DD water with dye solution	Time period
1	Cationic	Methylene blue	50	40 ml	90 minutes
2	Anionic	Eosin solution	38	40 ml	60 minutes

Table 3- DETAILS OF DYE DEGRADATION

3.7 Study over thermal properties.

The Fenugreek seeds are founded to be burned out when the temperature is raised above 200°C, [21]. Therefore, the Thermal withstand range for fenugreek seeds in Nanoscale are analysed for the first time with a Thermogravimetric analyser, and the TGA results are shown in the figure 11.

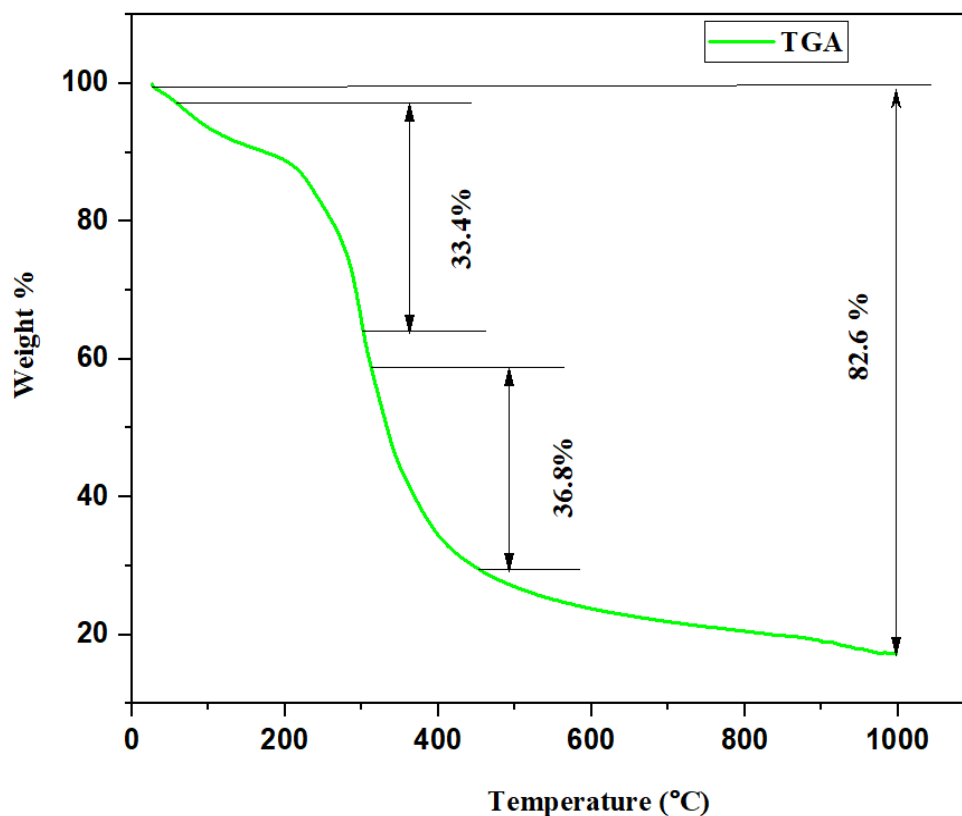


Figure 11- TGA OF FENUGREEK NANOPARTICLES

The below listed are the principle components, minerals and Vitamins contents which is present in fenugreek seed per 100 gram [21].

S.NO	Components	Content
1	Moisture (%)	13.7
2	Protein (%)	26.2
3	Fat (%)	5.8
4	Minerals (%)	3.0
5	Fibre (%)	7.2
6	Carbohydrates (%)	44.1
7	Calcium (mg)	160
8	Phosphorus (mg)	370
9	Iron (mg)	14.1
10	Carotene (μg)	96
11	Thiamine(mg)	0.34
12	Riboflavin (mg)	0.29
13	Niacin (mg)	1.1

Table 6- LIST OF COMPONENTS PRESENT PER 100G OF FENUGREEK SEED

In addition to the reference, the elemental analysis has been taken for the synthesized fenugreek nanoparticles.

3.7.1 Elemental Analysis

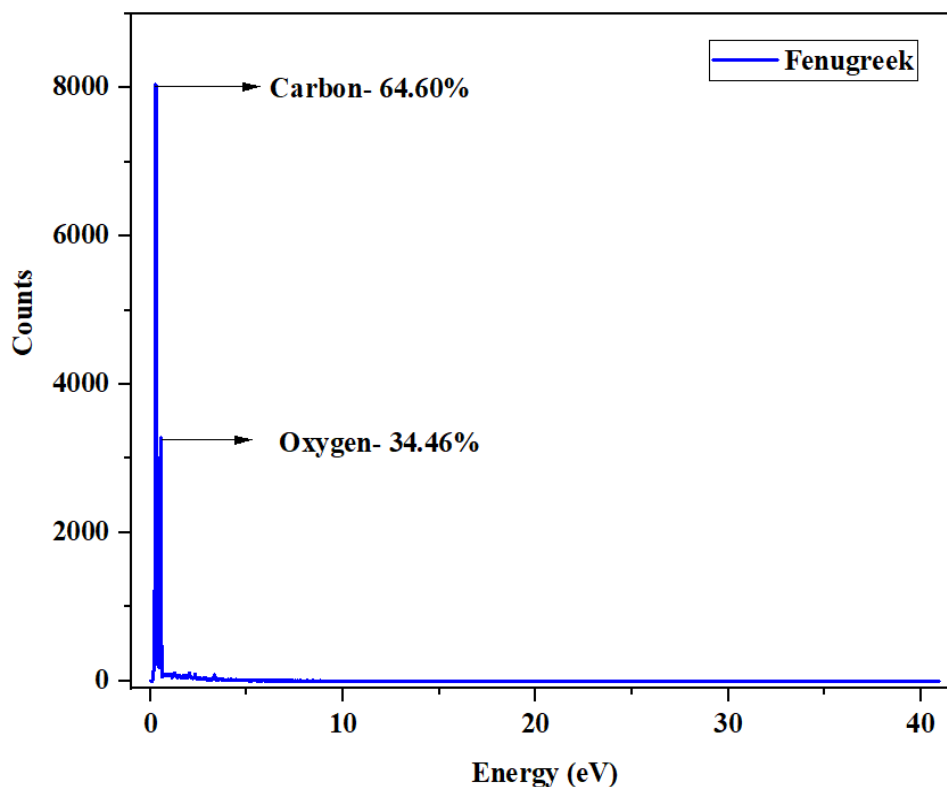


Figure 12- ELEMENTS PRESENT IN FENUGREEK NANOPARTICLES

The presence of elements in fenugreek nanoparticles is listed in the below table:

S.NO	Name of the element	Weight %	Atomic %
1.	Carbon	57.18	64.60
2	Oxygen	40.63	34.46
3	Magnesium	0.52	0.29
4	Phosphorus	0.51	0.22
5	Sulphur	0.31	0.13
6	Potassium	0.85	0.29

Table 7- List of elements present in fenugreek nanoparticles

The weight loss occurred at 302 and 451°C are due the loss of principle components which is listed in the Table 6, and when the temperature is raised further above from 451°C the nanoparticles are capable to withstand the temperature up to 1000° C with a total weight loss percentage of 82, it is due to high carbon content of almost 57.18% present in fenugreek nanoparticles.

3.8 SEM image of Fenugreek nanoparticles

The SEM images for fenugreek nanoparticles are captured for the first time.

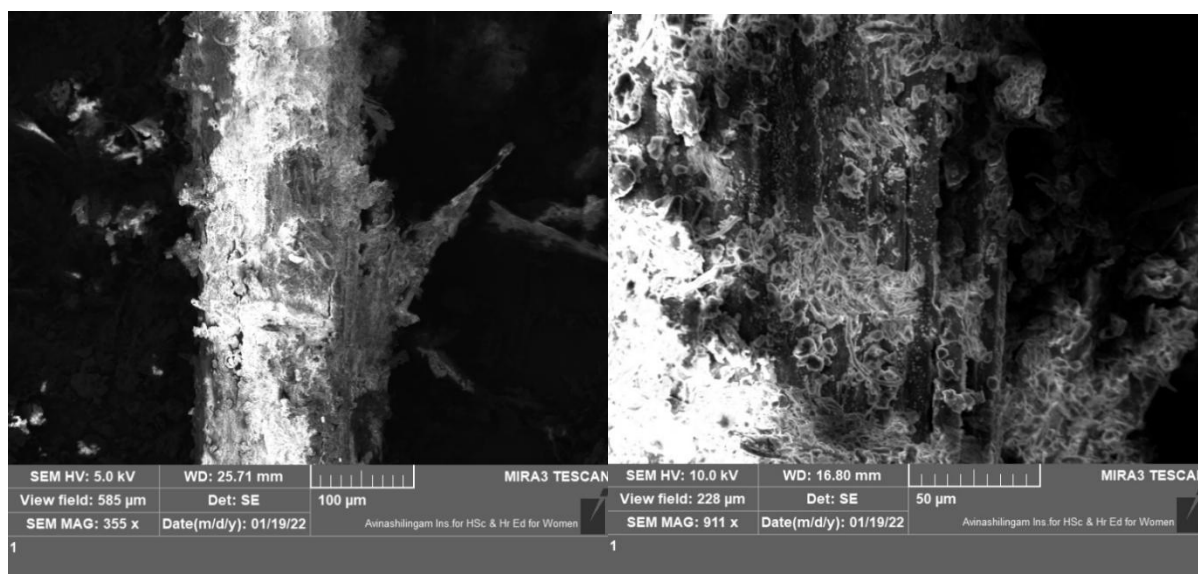


FIGURE 13 A & B - MUCILAGINOUS FIBRE

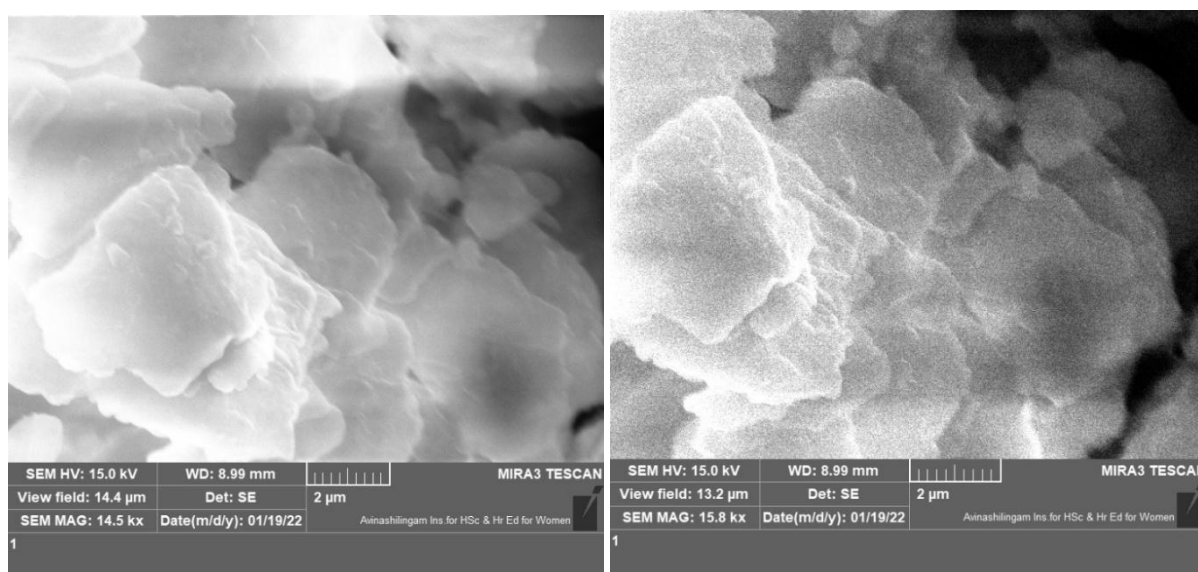


FIGURE - 14 C&D - SURFACE IMAGES OF THE FIBRE

The Figure 13A shows images of mucilaginous fibre and Figure 13B shows ‘N’ number of mucilaginous fibre surrounded by minerals and vitamins. Figure 14 C&D shows the surface images of the fibre where the surface looks to be very soft and encapsulated in shape and each capsule are closely packed one to one. From the surface images it seems like mucilaginous fibre is not willing up to give up its softness nature and the proof is, when this fibre immersed in water it dissolves in it and

gives raise to galactomannan, this galactomannan seems to possess a soft and sticky outer surface, the reason for this softness is due the soft nature of the Fibers as shown in the SEM images.

4. Conclusion:

The study proves that fenugreek nanoparticles have the potential to degrade both type of dyes (cationic and anionic dye) at normal room temperature without giving any external stimuli, this is the greater advantage of this study, the fenugreek nanoparticles are not subjected to any kind of irradiation such as sunlight or UV light for dye degradation, which makes the fenugreek nanoparticles a unique one in dye degradation, ready to be used for dye degradation at any time and at any condition. The Thermogravimetric study proves that it can withstand the temperature up to 1000°C due to the presence of various principle components likes vitamins and other minerals and high carbon content inside it.

The study has been carried out with 50mg of fenugreek nanoparticles for both type of dye degradation, the results show the dye degradation percentage of 50% for methylene blue and 38% for eosin dye and the reaction time is between 60 to 90 minutes, If the concentration of the fenugreek nanoparticles is further increased from 50mg to several grams a higher % of dye degradation can be achieved and the proof is this research work.

Similar to fenugreek seed many seeds and leaves have a unique natural property when these seeds and leaves are converted to nanoscale and tested for its nature properties in nanoscale a revolutionary composite material can be developed in future.

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Availability of data and materials

The data sets or analysed during the current study are available from the corresponding author on reasonable request.

Credit authorship contribution statement

Gokularamana.N: Conceptualization, Material preparation, Data collection, Data analysis, Writing – original draft. Dr.S.Satheeskumar: Conceptualization, Supervision, Writing – review & editing, Validation.

Declaration of Competing Interest

The authors affirm that they have no known financial or interpersonal conflicts that would have seemed to have an impact on the research presented in this study.

Data availability

Data will be made available on request.

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