Optimization of Parameters of Green Synthesis of TiO_2 NPs for UPF Analysis of Cotton Fabric

Singh Amrita, Gaud Brijesh and Jaybhaye Sandesh*
Research Lab, Department of Chemistry, B. K. Birla College, Kalyan, Maharashtra, INDIA
*jaysandesh@gmail.com

Abstract
The synthesis of metal oxide nanoparticles (MONPs) by biological method using plant extract is economical, ecofriendly and efficient. Nowadays, metal nanoparticles (NPs) have attracted great scientific interest due to their unique physicochemical properties. In present work, we report the qualitative as well as quantitative methods for synthesis of TiO_2 NPs using biological method. Optimization of parameters like pH, concentration of Metal Salts and reaction time for TiO_2NPs was carried by using Taguchi orthogonal array. TiO_2NPs were characterized using UV–Visible spectrophotometer, X-ray Diffraction, Scanning Electron Microscope, Transmission Electron Microscope, Particle Size Analyzer (CPS). The size of synthesized TiO_2NPs was 30-50 nm and spherical in shape.

TiO_2NPs synthesized at Optimum condition were incorporated in cotton fabric. UV protection Factor was analyzed before treatment and after treatment with NPs of cotton fabric.

Keywords: Metal oxide NPs, Biological method, Taguchi orthogonal array, TiO_2NPs, UV protection Factor.

Introduction

Different methods for the synthesis of metal oxide NPs have been reported such as Sol–Gel, Solvo-Thermal, Hydrothermal, Solution-Combustion and Sonochemical methods. Among various methods available for the synthesis of metal NPs, laser evaporation and chemical reduction are the major ones. In laser evaporation methods, use of costly and sophisticated instruments employ high temperatures and yields of NPs are quite low. Similarly, chemical reduction method may end up with the some toxic chemical species. This may have some adverse and cost effects in NPs applications.[1,2]

This attracts the researchers in the field of nanoparticle synthesis and applications to utilize some novel, eco-compatible and green methods for synthesis of NPs. Synthesis of metal NPs mediated through plant is a greener route and is considered better choice among the different biological methods as they provide a simple, cost-effective, stable for long time, reproducible and previously unexploited method, ecofriendly, clean with safe and cost effective utilization and beneficial for the large scale production.[3] Taguchi is an engineering method for product or process design that focuses on minimizing variation or sensitivity to noise. Taguchi designs are balanced, that is, no factor is weighed to a greater or lesser degree in an experiment, thus allowing each factor to be analyzed independently of the other factors. The major concepts in Taguchi experimental design are: (1) factor: studied variables affecting the response of an experiment (2) level: values of studied factors in an experiment (3) orthogonal array (OA): in experimental design, there is different set of OA, for example, L9 array is used for 3 factors each in 3 levels (4) optimum condition: optimum conditions to be found involve three major categories (a) the maximum value is the best, (b) the minimum value is the best and (c) typical value is optimum one.

We report a novel, environmental friendly, fast crystallization, cost efficient, low waste production and green synthesis of TiO_2 NPs and optimized parameters using Taguchi optimization. Parameter optimized are pH of plant extract, reaction time with different concentration of Titanium Tetrachloride salts by using extract of different plant extract like *hibiscus rosasinensis* (HRS), *azadirachta indica* (Neem) and *ocimum tenuiflorum* (Tulsi) as natural reducing agent.

The optimized samples were characterized by CPS Particle size analysis, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and High-resolution transmission electron microscopy (HRTEM).

Material and Methods

Materials: All chemicals used are of analytical grade. Leaves extract of *hibiscus rosasinensis* (Gurhal), *azadirachta indica* (Neem) and *ocimum tenuiflorum* (Tulsi) for synthesis of TiO_2 NPs were collected from B. K. Birla College, Kalyan, Thane, Maharashtra.

Methods:

Preparation of Plant Extract: 10 gm leaves of *hibiscus rosasinensis* (Gurhal), *azadirachta indica* (Neem) and *ocimum tenuiflorum* (Tulsi) were washed with distilled water to remove surface contamination and crushed. The paste of leave was refluxed by adding 100 ml of distilled water at 100^0C for 60 minutes to obtain saturated solution of leaves extract. Reflux solution was cooled at room temperature and filtered with Whatmann filter paper no.41. Filterate was used as plant extract.

Synthesis of TiO_2 NPs: 10 ml of $TiCl_4$ with different concentration was added with 1:1 ratio of different plant extracts having different pH at different reaction time. Different parameters were optimized for synthesizing TiO_2 NPs including pH, reaction time, temperature and concentration of $TiCl_4$.

Orthogonal array and characterization techniques

Orthogonal array: In this work the TiO_2 NPs obtained were characterized. Table 1 shows the parameters and levels used in this experiment. The particle size of TiO_2 NPs were characterized using following technique.

CPS (Particle Size Analyzer) analysis: Particle size analyses were carried out using CPS Disc Centrifuge Model No.12000 UHR of CPS Instruments.INC.

X-Ray Diffraction (XRD) Analysis: XRD measurements were performed on MiniFlex machine unit with Cu-Kα radiation (λ = 1.54178 Å) at 40 kV and 15 mA and scan-speed of 04.00 °/min.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS) analysis: SEM was done on a Jeol JSM -7600F FEG-SEM model no.JSM-7600F with SEI resolution1.0nm at 15 kv,1.5nm at 1 kv, in GB mode having magnification as low: 25X to 10,000X and high: 100X to 1,000,000X with accreting Voltage 0.1 to 30 kv and Probe Current Range 1 pA to ≥ 200 nA.

Results and Discussion

Taguchi design and orthogonal array: Taguchi robust design method was used to identify the optimal conditions and to select the parameters having the influence on the particle size of TiO_2 NPs. The structure of Taguchi's orthogonal robust design and the results of measurement were shown in table 2 and the smallest values of particle size (37 nm) were shown in experiment no. 7. The values of S/N ratio of Taguchi method were used to measure the quality characteristic deviating from the desired value. The S/N ratios are different according to the type of characteristic.

In the case that smaller characteristics are better, the S/N ratio is defined as: S/N Ratio [dB] $=-10 \log[(y21+ y22+ y23+\cdot\cdot\cdot)/n]$[7] where yi is the characteristic property and n is the replication number of the experiment. Table 2 shows the S/N ratio for particle size. The mean S/N ratio for each level of the parameters is summarized and the S/N response table for particle size is shown in table 3. As shown in table 3, the data of (max.−min.) of parameter D i.e. reaction time is the highest value. Therefore, it can be found that reaction time is the significant parameter affecting particle size.[8]

The greater is the S/N ratio, the smaller is the variance of particle size around the desired value. Therefore, the optimum condition is A3, B1, C3 and D3. In other words, based on the S/N ratio, the optimal condition for particle size is the concentration at 2.5 mM $TiCl_4$.[9]

Table 1
Parameters and Levels for optimization

Parameters		Level 1	Level 2	Level 3
A	Metal Salts Concentration	10	5	2.5
B	pH of Plant Extract	5	7	9
C	Plant Extract (Leaves)	Hibiscus	Neem	Tulsi
D	Reaction Time	30	60	90

Table 2
Experimental measured values and S/N ratio for particle size of TiO_2 NPs (Taguchi orthogonal array table of $L_9(3^4)$)

Level	Concentration (mM)	pH	Plant Extract	Time (min)	Average Particle Size (nm)	S/N ration of Size
L1	10	5	H	30	163	-44.2438
L2	10	7	N	60	152	-43.6369
L3	10	9	T	90	57	-35.1175
L4	5	5	N	90	47	-33.442
L5	5	7	T	30	70	-36.902
L6	5	9	H	60	160	-44.0824
L7	2.5	5	T	60	38	-31.5957
L8	2.5	7	H	90	40	-32.0412
L9	2.5	9	N	30	275	-48.7867

Table 3
S/N response table for particle size

Parameter		Level			Data of (max.−min.)
		1	2	3	
A	Concentration (mM)	-44.999	-38.1421	-37.4745	7.52450
B	pH	-36.4272	-37.4883	-42.6622	6.23503
C	Plant Extract	-40.1225	-41.9552	-34.5384	5.58406
D	Reaction Time (min)	-43.3108	-39.7717	-33.5336	9.77727

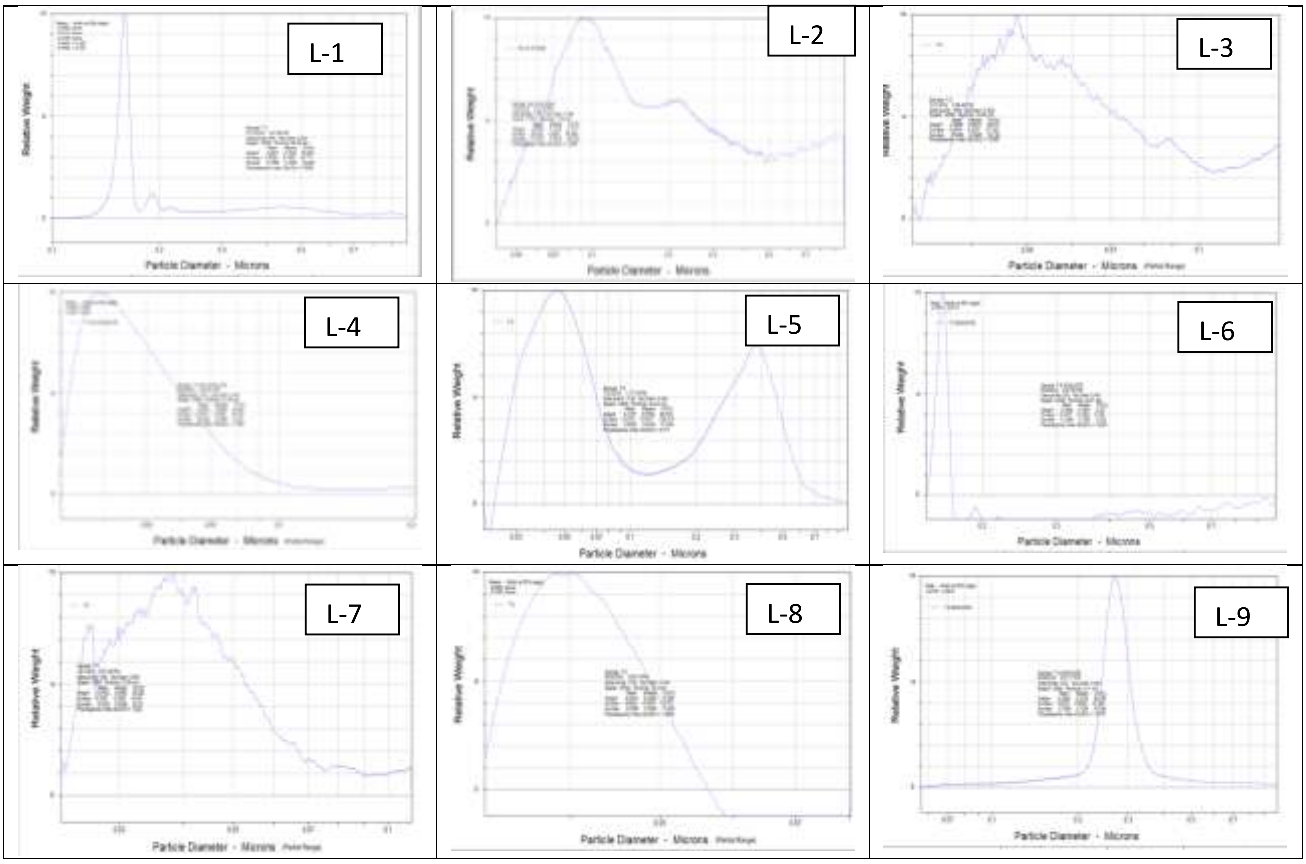

Fig. 1: Optimization of Particle size was analyzed by CPS particle size analyzer of each test

Characterization of TiO_2 NPs

Particle Size Analysis: Optimization of particle size was analyzed by CPS particle size analyzer of each test (L-1 to L-9) for TiO_2 NPs of all L9 (3^4) test as shown in fig.1.Particle size distribution of the TiO_2 NPs obtained at optimal conditions is characterized as follows:

X-Ray Diffraction (XRD) Analysis: Fig. 2 shows the XRD pattern of the prepared powder at optimal parameter. The crystallite size of the particles has been estimated from the Debye–Scherrer's equation using the XRD line broadening as follows:[10,11]

$$D / (2\theta) = \frac{k\lambda}{\beta \cos\theta}$$

The XRD pattern of TiO_2NPs obtained from green synthesis is shown in fig. 2. The result showed that the structure was in tetragonal structure and these results were in good agreement with JCPDS card number 96-901-4506. Peaks were absorbed at 29°, 40°, 48°, 55°, 67° and 75° along with Miller indices values (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4) and (2 1 5) respectively.[12]

where D is the average crystallite size of the particles, K- is Debye Scherrer's constant (=0.94), λ is the wavelength of the CuKα-radiation (=0.154 nm), β is the full width half maximum (FWHM) of the peak, θ is the Bragg's angle. The average crystallite size was measured as 20 nm using the above formula.

SEM and EDS analysis: The grain size, shape and surface properties like morphology were investigated by the SEM shown in figure 3. This image was observed in the magnification of 1,50,000. The TiO_2 NPs were showing spherical shape structure. The size was ranging from 14 nm to 30 nm. EDS for detection of and conformation of TiO_2 NPs shows an SEM image of the area being analyzed by EDS. The EDS spectrum shows the presence of TiO_2 NPs as in figure 3.

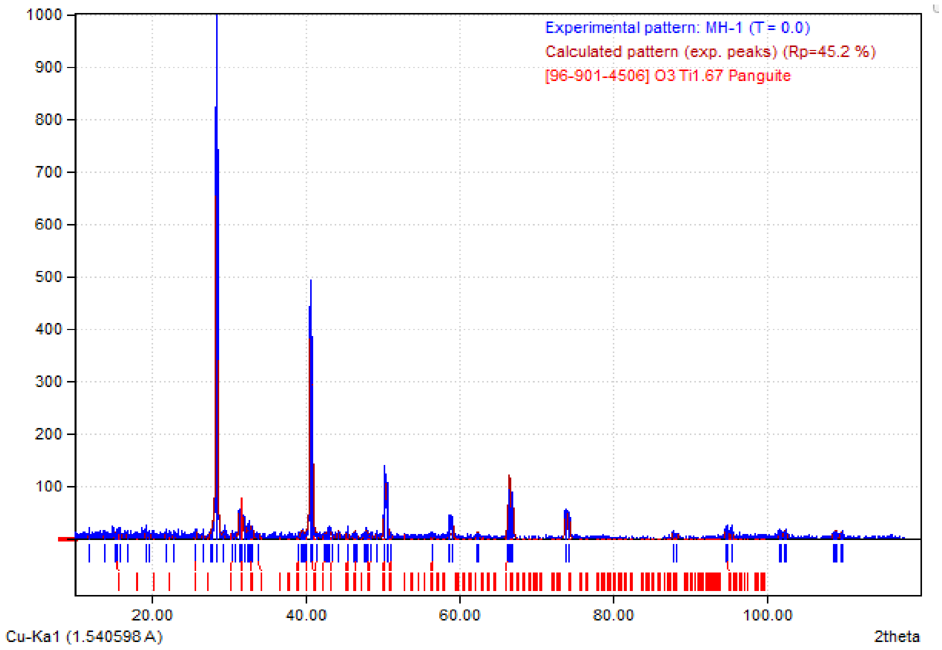

Fig. 2: XRD Spectra of TiO_2 NPs

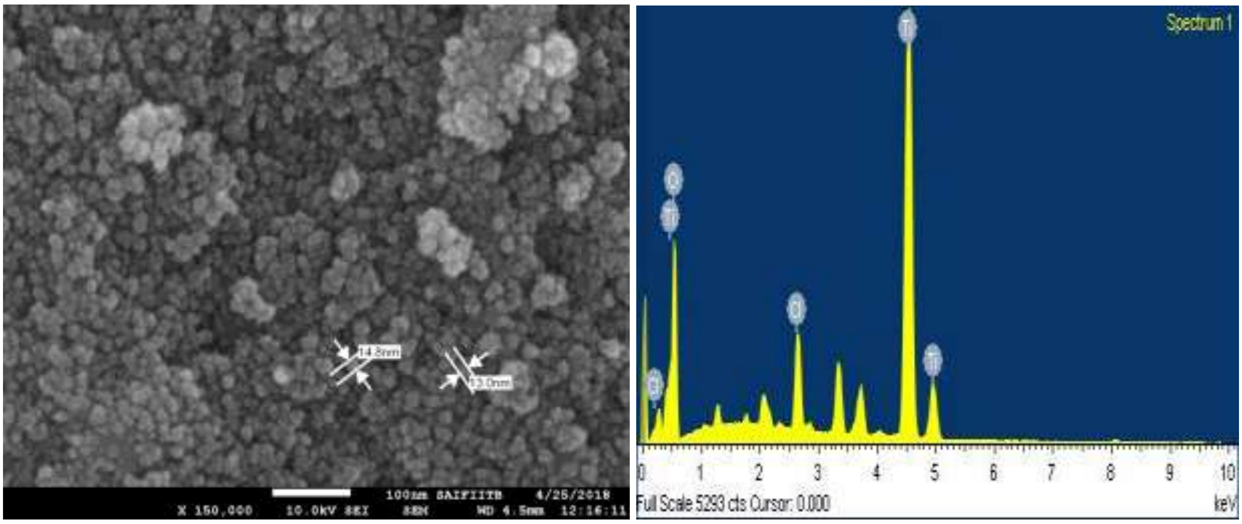

Fig. 3: SEM and EDX Spectra of TiO_2 NPs

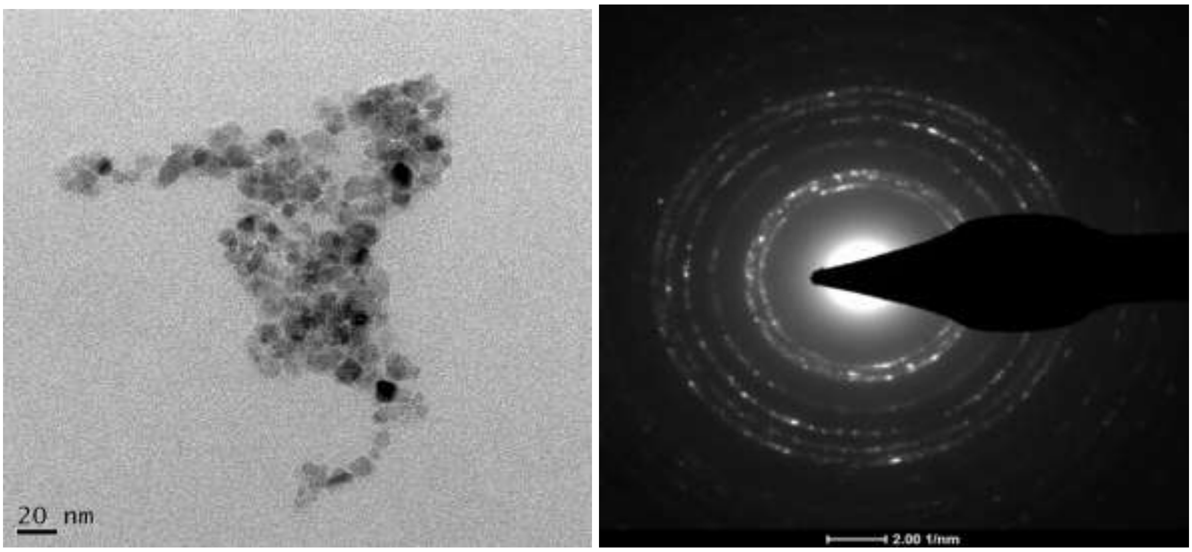

Fig. 4: TEM image and SEAD image of TiO_2 NPs

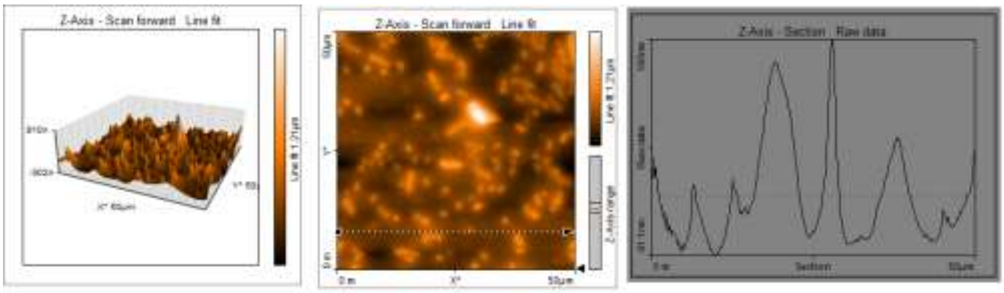

Fig. 5: AFM image of TiO_2 NPs

Transmission Electron Microscopy: The morphology and structure arrangement were observed by TEM. The TEM image was shown in figure 4. TiO_2 NPs were found to be spherical in shape. Select-area electron diffraction (SAED) image of HR-TEM indicated crystalline nature of TiO_2 NPs.

AFM analysis: Fig. 5 shows size and shape of the NPs obtained directly from tip-corrected AFM measurements and the shape of the NPs is estimated on the basis of AFM images and lines cans. The tip-corrected measured the size of 20–40 nm, average Surface roughness is 52.8 nm and spherical in shape.

Loading of TiO_2 NPs on Cotton Fabrics and UPF Analysis: 0.010 gm of TiO_2 NPs was sonicated with 100 ml of distilled water for 30 min with amplitude of 45 %. Cotton fabrics with maximum dimensions of 5 cm × 5 cm were dipped in disperse TiO_2 NPs solution and sonicated for 30 min with continue shaking for 24 h and dried at 70 ºC. [13]

The UPF analysis was done in ICAR-Central Institute for Research on Cotton Technology (ICAR-CIRCOT) using UV transmittance analyzer. UV protection Factor (UPF) was analyzed before treatment and after treatment with NPs of cotton fabric.

Transmission measurements were made in the 290-400 nm range with 1 nm step. UPF was calculated according to:

$$UPF=\frac{\sum_{290}^{400} E_\lambda S_\lambda \Delta_\lambda}{\sum_{290}^{400} E_\lambda S_\lambda T_\lambda \Delta_\lambda}$$

where S_λ is the solar spectral irradiance at noon for a typical summer's day, E_λ is the CIE erythemal spectral effectiveness, T_λ is the spectral transmittance of each fabric sample and Δ_λ is the wavelength step. The nine measurements of each sample were averaged and standard deviation was calculated.[14,15] UPF measures how much of the sun's UV radiation is absorbed or "blocked" by fabric UPF ratings range from 15 to 50 and a higher UPF rating indicates greater protection[16] as shown in table 4.

The average transmittance percentage of fabrics is ca. 35% for both UV-A and UV-B. As seen in table, the blocking percentage of the coated block 55+ % of coated fabrics shows that the percentage of blocking UV-A and UV-B radiation is higher than that of cotton fabric even after 25 washings with water.

Conclusion

In this study, we demonstrated Taguchi robust design method with L9 orthogonal array implemented to optimize experimental conditions for the preparation of TiO_2 NPs. Reaction time was main parameter having significant effect on particle size. using optimal conditions obtained by Taguchi method. The green synthesis of using optimal parameters gives spherical shaped NPs. NPs and thus were characterized by particle size analyser, XRD, SEM, TEM and EDX.

Table 4
The average transmittance percentage

Sample	UPF Ratting
Cotton fabric	35 %
Coated fabrics with TiO2 NPs	50+ %
After 25 % washing with water	50+ %

The synthesized TiO_2 NPs were found to be spherical in shape and the particle sizes were in the range of 14-30 nm. The UPF analysis shows the enhancement of UPF after incorporation of TiO_2 NPs into cotton fabric even after 25 washings with water.

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