

Comparative Study on Structuring and Photocatalytic Activity of Nano Titania Embossed with Organic Extracts

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ABSTRACT: Several extensive research studies have explored the advantages of green templates in the synthesis of structure and morphology-controlled photocatalytic nanomaterials. This study compares the potential aspect of Zingiber rhizome Extract (ZE) and Tapioca Starch extract (TS) in modifying the surface and optical properties of Titania NanoParticles (TNP) synthesized by the sol-gel technique. The synthesized nanocatalysts were characterized using various physicochemical techniques. While zingiber extract promotes effectively favored the formation of dual anatase and rutile phases, tapioca extract ended with single anatase phase titania, which was examined for the degradation of Congo red in the presence of sunlight. The photo mineralization and recyclability of catalysts have been evaluated through Total Organic Content analysis. The easy recovery and reusability of biosynthesized nanocatalysts with good control over the grain size, enable them to be an implicit novel green template in the successful synthesis of photoactive mesoporous nano titania.

KEYWORDS: Nano Titania; Congo red; Photocatalyst; Degussa-P25; Sol-gel technique.

INTRODUCTION

The textile industries found to exploit different forms of water ecosystems by discharging huge volumes of polluted water with toxic chemical compounds and thereby become responsible for various health issues [1] due to the degradation of dyes and pigments [2] Hence wastewater treatment has become mandatory to solve various health and industrial issues. In recent years Advanced Oxidation Processes (AOPs) have been developed to meet the present needs and expectations in the field of water treatment techniques. Hydroxide radicals generated during the process completely destroy the pollutants in water and for the past two decades the process was dominated by the employment of semiconductor metal oxides and sulphides as photo

catalysis. For instance, titanium dioxide nanoparticles with a wide band gap of 3.2 eV are reported to be an effective photocatalyst and used for the treatment of organic compounds [3] and dyes [4] which are major contaminants in industrial effluents. Titanium dioxide nanoparticles being a dominant photocatalyst, the synthesis, physicochemical and surface properties of the same have become quite interesting and significant. The control over the shape of a synthesized photocatalyst is highly claimed to enhance the rate of adsorption of organic pollutants on its surface. Hence effective synthetic route is necessitated [5] for the synthesis of mesoporous nano titania with high surface area, low porosity, reduced crystallite size, and energy band gap [6].

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Out of several methods available for the synthesis of nano titania sol-gel method is likely to be more suitable and advantageous being less expensive, simple, and can be processed out at ambient temperature [7] providing adequate control over their shape and structure under different parameters. Further, the above technique has been recommended by the inclusion of bio extracts as templates to produce nanocatalysts with controlled porosity, homogeneity, and grain size to satisfy desired structural and surface characteristics. The various studies have thrown a light on the contribution of different inorganic materials as templates to impart necessary modification on their characteristics, as an alternative to doping with metals, nonmetals, and surfactants [8-10]. Nano titania photo catalysts synthesized utilizing templates like PEG 1000 [11], CTAB [12], Pluronic P-123 [13] have been reported and paved way for visible light mediated photo catalysis to back up the above process for efficient photodegradation and photo leaching of different dyes after exploiting solar energy available in plenty [14].

At this context many attempts have been carried out to develop novel, eco-friendly and less complicated methods free from biological risks [15]. Recently the, green synthesis or biogenic synthesis of mesoporous nano titania using plants and their products like Chitosan [16], lotus root [17], gum [18.], bamboo cap [19.], Rice straw [20] has drawn much attraction and shown better results over other physical and chemical methods. In this study the degradation of azo dye namely Congo red, discharged mainly from textile, plastic and leather industries was chosen as a model pollutant.

In this paper titania nano particles were synthesized by sol-gel technique using zingiber and tapioca extract as bio templates under the principles of green chemistry as an initial attempt and characterized using spectral techniques like XRD, FT-IR, TGA, DRS-UV, BET, UV-VIS, SEM and TEM etc. It is found that both the extracts have shown their marked influence in the modification of grain size, phase composition and morphology of the catalysts as they were employed.

Zingiber extract has various components which depend on its origin and freshness of the rhizomes confirmed with the presence of organic functional groups like Carbohydrates, Fats and Proteins present in the extract [21]. The primary and secondary cell wall of carbohydrate

polymers contains cellulose, hemicelluloses, pectin and lignin imparting mechanical strength to the tissues [22], is also rich of polyphenolic compounds and flavonoids such as gingerols, zingerone, terphenol, paradol, terpenes, geraniol, alpha zingiberene etc. From the recent studies it is noted that ginger extract was used in the synthesis of gold, silver and zinc oxide nano particles [23,24], and the present study was undertaken for the first time to evaluate the efficacy of zingiber extract in the green synthesis of titania nano particles [24].

A natural tapioca extract rich of tapioca starch created an interest in present days among commercial starches as they contain low amylase content. Presence of low level residual materials, amylose and amylopectin of high molecular weight improved its industrial applications and as a starting material for physical and chemical modifications [25]. Added to this, above starch with properties like lowering of surface tension, control of particle size and aggregation has been reported as a bio template in the synthesis of ZnO nano particles and employed in the photodegradation of methylene blue [26].

This work presented the successful synthesis of mesoporous crystalline titania nano particles using organic bio materials mentioned above as templates for the first time and also investigated in detail their photocatalytic activity against Congo red, an azo dye in the visible region for the first time.

EXPERIMENTAL SECTION

Materials required

The reagents like Titanium iso propoxide (99%) and iso propanol (98%), HCl, NaOH were purchased from Sigma Aldrich. The zingiber rhizomes and tapioca pearls were obtained from local market. The sample organic pollutant Congo red dye was obtained from Reachem chemicals laboratory private limited, Chennai. Double distilled water was used in the preparation of experimental solutions.

Preparation of Zingiber and Tapioca biomass

Fine and fresh pieces of zingiber rhizomes were obtained from the market. The rhizomes were cut into pieces and washed repeatedly with pure water. The pieces were sun dried and hot air oven at 60° C. The dried rhizomes were grounded to a fine powder.

A 500 g of tapioca pearls were taken in a known volume of water and heated to 100°C for 1h. When the

mass became glassy, pasty and transparent, the contents were transferred to a clean plastic sheet and Sun-dried for 6 days. The dried pearls were grounded to a fine powder and stored in an air-tight container.

Preparation of photocatalysts

At room temperature, 9mL of Titanium iso propoxide (TTIP) is mixed with 60 mL of iso propanol under continuous stirring using a magnetic stirrer. The zingiber extract powder was dissolved in 50mL distilled water followed by 20% nitric acid and stirred vigorously for half an hour constantly. Then the later solution was added to the former drop by drop under stirring to get a colloidal solution. The resulting solution is kept for 12 h to get a gel. The solution is filtered and dried at 150°C in an air oven for 2 h. The sample obtained as a dry powder was calcined at 500°C for 10 h. The same procedure is repeated using tapioca extract without adding 50% nitric acid. The calcined samples were labeled as NTZ0.5, NTZ1 and NTZ1.5 and NTT1, NTT1.5, NTT2 denoting the weight of Zingiber and Tapioca extracts to be 0.5, 1 and 1.5 g respectively. Nano titania prepared in the absence of extracts were taken as control and labeled as NT.

Characterization of the synthesized catalysts

The synthesized calcined samples were analyzed using an X-ray diffractometer with Cu K α ($\lambda=1.546\text{\AA}$) radiations in 2θ range from 20° to 80° with a scan rate of 2° per minute at room temperature in order to assess their crystallite size and structural properties. A Perkin-Elmer spectrometer using KBr pellet technique was used to study FT-IR. About 20mg of the sample was made into a pellet along with special grade KBr using a hydraulic press. The synthesized samples were subjected to scanning between 4000-400 cm^{-1} . UV-Visible diffused reflectance spectroscopy analysis of the synthesized titania samples was performed using Shimadzu UV 2450 with BaSO $_4$ as a reference. The band gap energy was calculated using the formula, $E_g=hc/\lambda$. Tauc equation (Tauc *et al.* 1966) was used to calculate the band gap energy of the synthesized photocatalyst:

$$(\alpha h\nu)^n = \text{const} (h\nu - E_g)$$

Where α - is the absorption coefficient, $h\nu$ - is the photon energy, and n - the type of electronic transition,

taken as 2 for directly allowed transitions. Based on nitrogen adsorption-desorption isotherms, the BET surface area, pore volume, and BJH pore size distribution were analyzed using a Quadrasorb surface analyzer. Scanning Electron Microscope Quanta 200 ESEM equipped with energy dispersive microanalysis was used to study the morphology and chemical composition of the synthesized samples. The thermal stability and the temperature of degradation of the synthesized samples were analyzed using a thermal analyzer SDT Q 600 V8. The degree of mineralization of Congo red was estimated from the total organic carbon (TOC) content using an Aurora TOC analyzer.

RESULTS AND DISCUSSION

Thermo gravimetric analysis

The thermogram obtained from the thermo gravimetric analysis of as-synthesized NTZ1 and NTT1.5 nano particles synthesized using zingiber and tapioca extracts has shown the decrease in weight with the increase in temperature is shown in Fig.1. The initial stage of weight loss from 100 to 180°C around 10 to 20% was due to the evaporation of moisture and other volatile species adsorbed from the surface [27]. The next stage of weight loss from 200 to 480°C around 4% was due to the decomposition of organic compounds like poly phenols, amines, polysaccharides and residues present in the extracts [28]. There is no considerable weight loss beyond 500°C and therefore 500°C was chosen as a calcination temperature.

X-ray diffraction analysis

Fig.2. shows the diffraction pattern samples of nano titania synthesized using zingiber and tapioca extracts. The different peaks were observed at 25.25°, 37.2°, 48°, 54°, 55°, and 61.5° confirmed the presence of anatase phase [10] in the samples. The debye-Scherrer formula was used to calculate the particle size using, $T = k\lambda / \beta \cos \theta$, Where 't' stands for particle size, ' λ ' the wavelength, ' β ' is the full-width half maximum of the diffraction peak, ' θ ' is the diffraction angle, 'K' is a coefficient and the values were reported in Table1 [29] The reduction in the crystallite size from 24nm in NT to 20.2 nm in NTZ1 and 22.6 in NTT1.5 showed that the growth of titania nano particles was hindered when the concentration of bio extract altered.

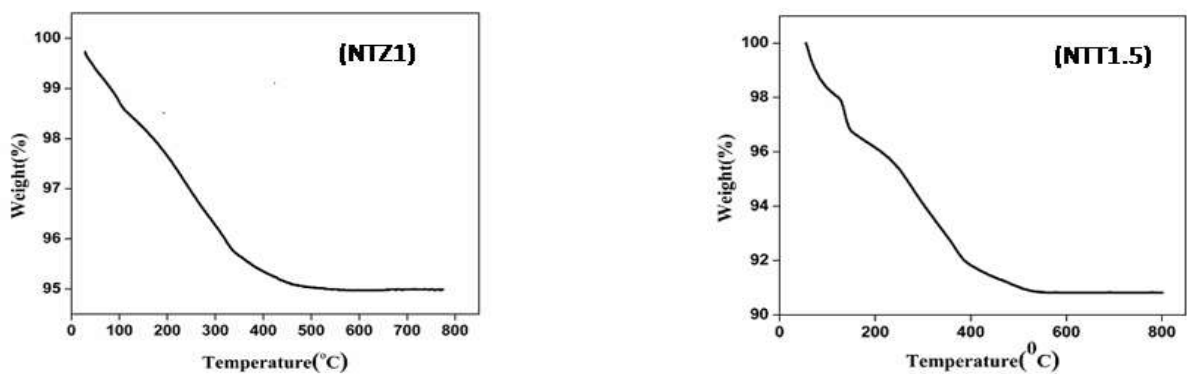


Fig.1: Thermogram of a) NTZ1 and b) NTT1.5.

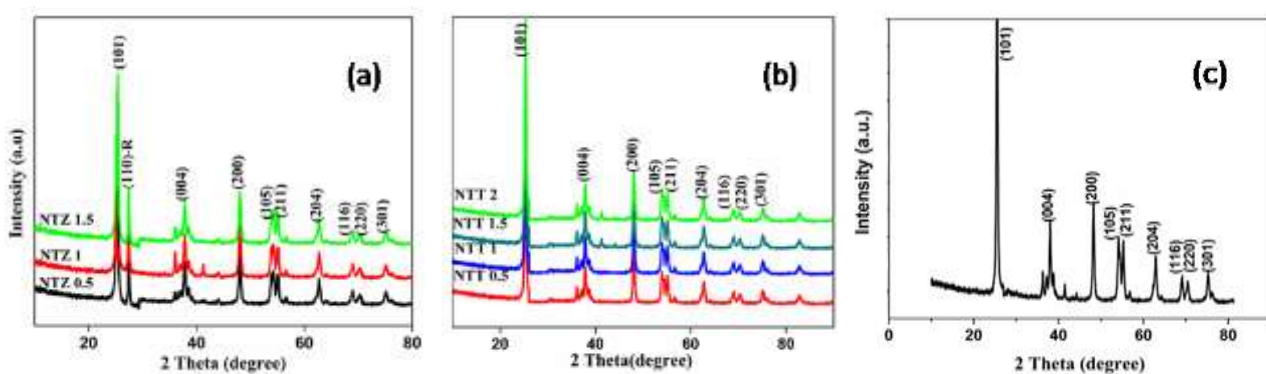


Fig.2: XRD analysis of a) as synthesized NTZ0.5, NTZ1 and NTZ1.5, b) as synthesized NTT0.5, NTT1, NTT1.5 and NTT2, c) controlled nano titania calcined at 500°C.

It is very interesting to note that increasing the percentage of zingiber extract resulted in the formation of a rutile phase at 27.8° along with anatase phases. The formation of the rutile phase was due to the addition of nitric acid which reduced the pH and consecutively a slow dissolution-crystallization of titania at 60°C led to a formation of the rutile phase [30] The strong interaction between the hydroxyl groups of the extract with titanium supposed to play an important role in stabilizing rutile phase [31] Titania photocatalyst with rutile and anatase phase compositions exhibited enhanced photocatalytic activity due to better charge carrier separation and reduction in the recombination of electron-hole pairs has been reported [32]

Optical properties

As shown in Fig.3 the absorption spectra of synthesized NTZ1 and NTT1.5 shifted to higher wavelengths, revealing a decrease in the band gap and

particle size. The band gap energies of NTZ1, and NTT1.5 were estimated to be 2.91 and 2.97eV most suitable for the photodegradation of organic pollutants under Sun light compared to NT with 3.12 eV which would respond only to UV light [4] The red shift might be due to the larger size of the semiconductor particle with its excitonic Bohr radius that leads to delocalization of LUMO in the conduction band already reported by the scientists [33].

FT-IR spectral analysis

FT-IR pattern of the synthesized NTZ1 and NTT1.5 samples are shown in Fig.4. The strong absorption bands of zingiber extract (4c) at 3445, 2920, 1656, 1464, 1381 and 1024 cm^{-1} were due to stretching vibrations of O-H, -CH₂, C-H, aromatic C-H in-plane, N-H, and C-N bonds showed the presence of various functional groups derived from heterocyclic compounds like alkaloids and flavonoids in the abstract [24] The corresponding peaks

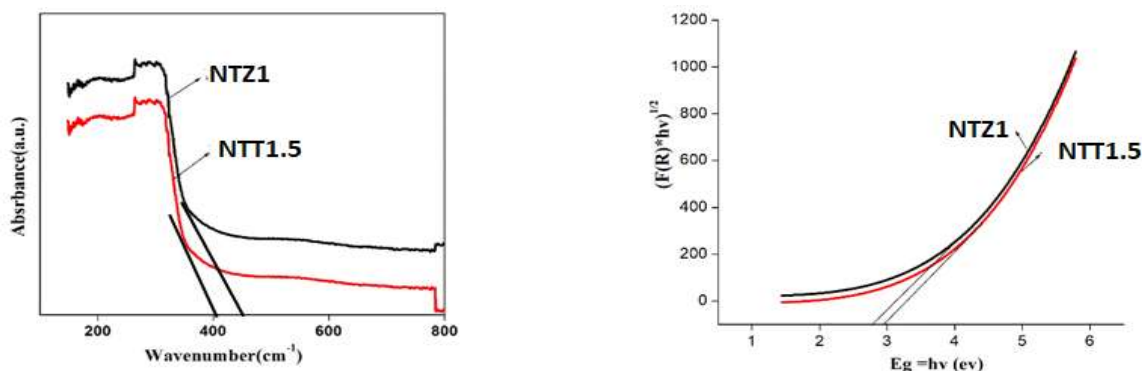


Fig. 3: UV-Vis spectra of (a) NTZ1, (b) NTT1.5 Calcined at 500°C.

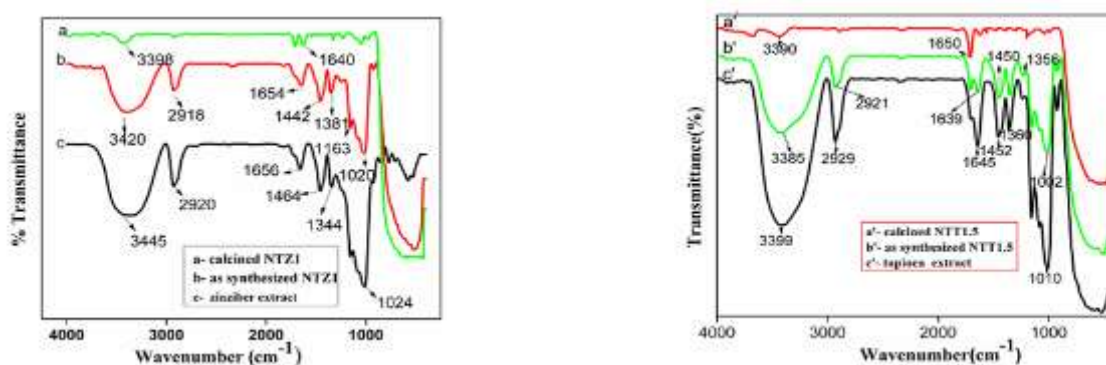


Fig.4: FT-IR spectrum of a, a') Calcined NTZ1, NTT1.5, b, b') as-synthesized NTZ1, NTT1.5, c, c') Zingiber extract (ZE) & Tapioca extract (TE).

like 3420, 2918, 1654, 1442, 1342, and 1020 cm^{-1} were shifted to the lower wave number in the as-synthesized NTZ1 sample (4b) suggesting that the different moieties have involved in complexation with the metal. The presence of alkenes in the zingiber root extract might have mediated the reduction of TiO_2 nano particles [34].

FT-IR spectra of the Tapioca extract sample (4c') show the absorption bands at 3399, 2929, 1645, 1452, 1380, and 1010 cm^{-1} found to be due to bending and stretching vibrations of C-O, and C-H bonds and also the ordered structure and amorphous nature of the starch [35,36] But in the case of as-synthesized NTT1.5 (4b') shifting of peaks towards the lower wave number indicates the weak interaction of functional group of the starch with the metal and oxygen at the surface [37]. The absence of characteristic peaks of zingiber and tapioca extracts (4a and 4a') around 3300, 1630 cm^{-1} showed the complete removal of the organic mass and the bands at 400-800 cm^{-1} showed the presence of hydroxide groups produced

during the solvent hydrolysis and Ti-O-Ti linkage [8]

Surface analysis

The nitrogen adsorption-desorption isotherm of as synthesized titania nanoparticles with zingiber and tapioca extracts of different ratios are shown in Fig.5a and 5b and the Barrett-Joyner-Halenda (BJH) analysis of NTZ1 and NTT1.5 are shown in Fig. 6a and 6b. Surface area, and pore size distributions of various synthesized samples were compared with controlled nano titania, is shown in Table 1. All the samples exhibited type III adsorption isotherm [4] with H3 hysteresis loop because of capillary condensation, have confirmed the presence of mesoporous materials in the catalyst channel [4] Further the isotherms were relatively flat ($P/P_0 \leq 6$) due to adsorption of samples in the micro pores of the catalysts and increased with the increase of relative pressure ($(P/P_0 \geq 7.5)$), so the adsorption ability was enhanced by mono layer or multilayer adsorption of nitrogen gas in the resultant catalysts [38].

Table 1: Physico-chemical characteristics of synthesized nano titania samples.

S.No.	Reference and Synthesized Materials	BET surface area(m/g) ^b	Crystalline size (nm) ^a	Average pore radius (A) ^c	Pore volume(cm/g) ^d
1	Degussa P25 (Ref.)	50	50	-	-
2	Synthesized Nano titania	NTZ	24	14	0.240
		NTT	23.8	12	0.25
3	Synthesized and Calcined	NTZ0.5	24.62	7.46	0.22
		NTT1	50	7.64	0.20
4	Synthesized and Calcined	NTZ1	60.8	9.62	0.30
		NTT1.5	55.2	9.46	0.36
5	Synthesized and Calcined	NTZ1.5	60	8.02	0.286
		NTT2	53.2	7.96	0.24

a) Average crystalline size was determined by XRD using Scherrer equation.

b) The BET surface area was determined from the linear part of the graph.

c) Calculated from the desorption branches of isotherms.

d) Estimated by BJH method.

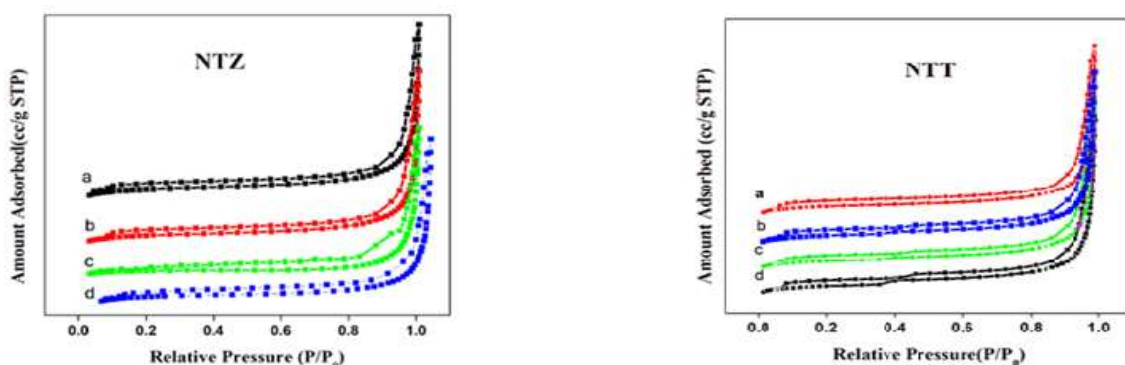


Fig.5: N₂ adsorption-desorption isotherms of a) as synthesized NTZ1, NTT1.5, b) as synthesized NTZ1.5, NTT2, c) as synthesized NTZ0.5, NTT1 and d) NT, calcined at 500 °C.

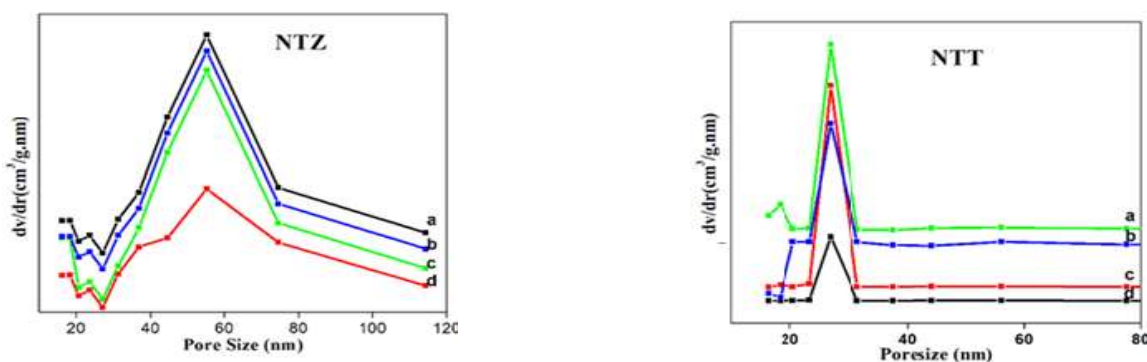


Fig.6: Pore size distributions of a) as synthesized NTZ1, NTT1.5, b) as synthesized NTZ1.5, NTT2, c) as synthesized NTZ0.5, NTT1 and d) NT, calcined at 500 °C.

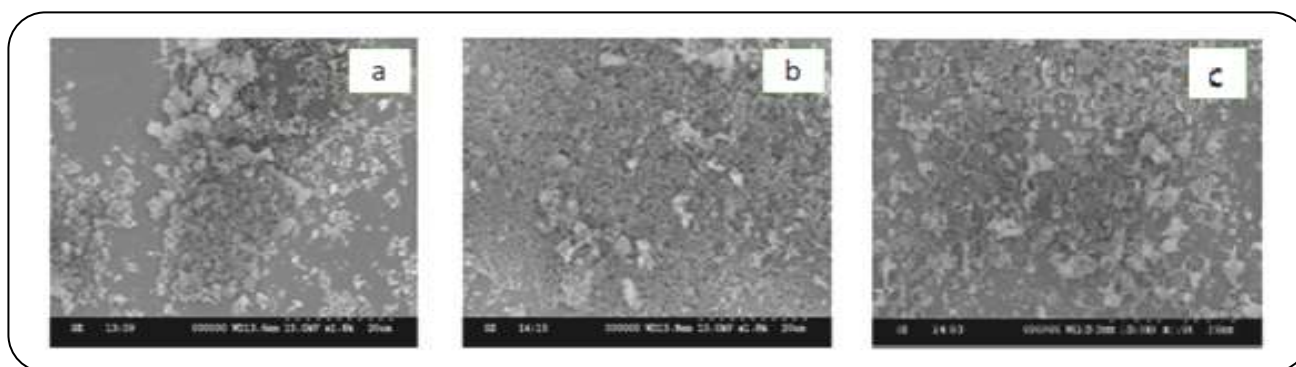


Fig.7: SEM images of a) Control NT b) NTZ1 and c) NTT1.5.

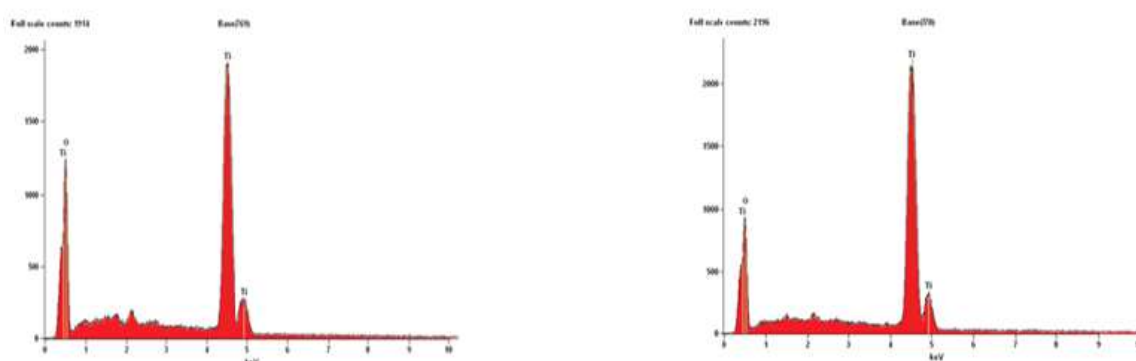


Fig.8: EDAX images of a) NTZ1 and b) NTT1.5.

The results indicated that the specific surface area of NTZ1 is $60.8 \text{ m}^2/\text{g}$ and that of NTT1.5 is $55.2 \text{ m}^2/\text{g}$, 10-20 % higher than other samples, and pore radius, pore volume, etc. also found to be increased by 10-15% which might be due to controlled aggregation of nanoparticles. The various things observed above supported that zingiber and tapioca extracts could be employed as surface-modifying agents in the synthesis of mesoporous titania nanoparticles and the photodegradation of an organic pollutant [39].

SEM and EDAX analysis

SEM images of as-synthesized titania nanoparticles by sol-gel method using zingiber and tapioca extracts calcined at 500°C is shown in Fig.7 compared to NT. While nano titania without organic mass showed agglomerated, irregular particles, NTZ1 and NTT1.5 depicted moderate, well-dispersed particles with better morphology. The degree of agglomeration depends on the addition of organic extracts like zingiber and tapioca extracts which makes the aggregation of molecules compact inhibiting the crystallite growth which is quite

evident from the XRD results [40] EDS pattern of NTZ1 and NTT1.5 in the Fig.8. have shown the presence of Ti and O peaks and nothing more. The bulk and the surface titania particles were evident from the intensified and less intensified peaks at 4.5 and 4.8 keV[37]The marked effects of larger surface area and minimum size were observed in the results of photocatalytic analysis of synthesized nanoparticles [41].

TEM analysis

From TEM analysis of as synthesized NTZ1 and NTT1.5 as shown in Fig.9, it is evident that added bio extracts thus played a vital role in the control of further growth of catalyst particles. This might be due to the controlled agglomeration of titania nanoparticles, more examined in the case of NTZ1 compared to NTT1.5 [41]

Photovoltaic activity

Effect of calcination temperature

The photodegradation ability of NTZ1 and NTT1.5 catalysts calcined at different temperatures in the range of 350 to 750°C is shown in Fig.10. In general, during

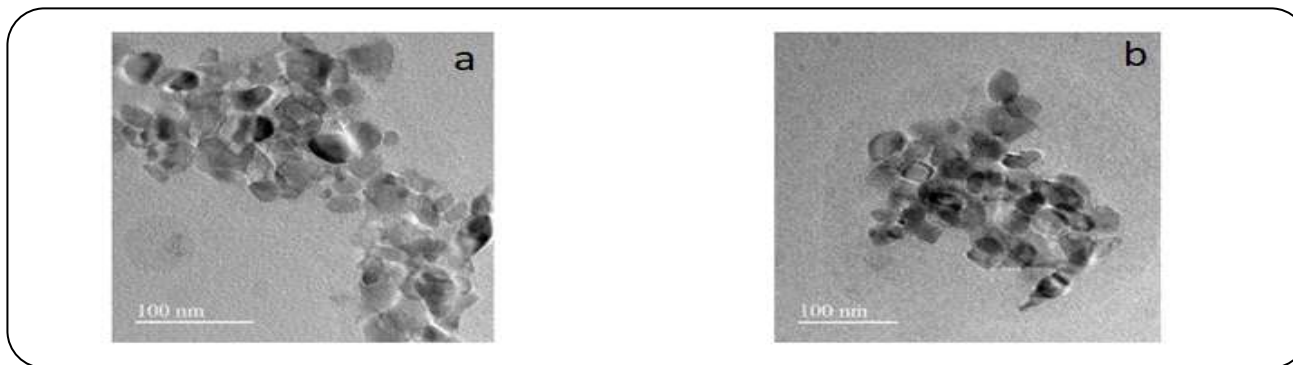


Fig.9. TEM images of a) NTZ1 and b) NTT1.5.

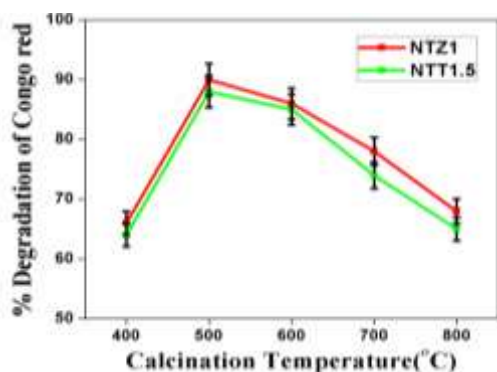


Fig.10: Effect of calcination temperature of a) NTZ1 and b) NTT1.5 on the photodegradation of Congo red [Congo red = 20µM, pH = 4, Amount of Catalysts =0.5 g/l].

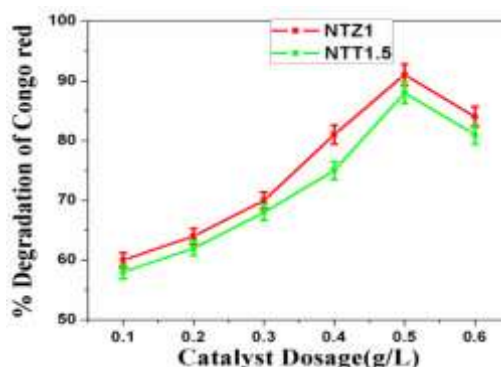


Fig.11: Effect of Catalyst Dosage of a) NTZ1 and b) NTT1.5 on the photodegradation of Congo red dye solution [Congo red = 20 µM, pH = 4, Amount of NTZ1&NTT1.5 =0.5 g/l].

calcination at higher temperatures dehydration of TTIP ($TiO_4H_8 \rightarrow TiO_2 + H_2O$) occurs producing more active sites and hence more adsorption and degradation [42] The maximum degradation of 90.4 and 89.6% of Congo red was observed for NTZ1 and NTT1.5 calcined at 500°C. But there is a decrease in degradation profile beyond 600°C which might be due to the phase transformation of the anatase phase to rutile at higher calcination temperature resulting in low degradation of Congo red [32] Therefore 500°C fixed as a calcination temperature was found to be optimal for efficient photocatalytic activity.

Effect of catalyst dosage

Fig.11. shows the effect of loading of NTZ1 and NTT1.5 on the photodegradation of Congo red. When the amount of catalyst were increased from 0.1 to 0.5 g/L, degradation percentage also increased from 60 to 90 % approximately, and the increase in the surface area resulted in more active sites made available more active sites on the

catalyst surface [43]When the catalyst dose is increased beyond 0.5g/l, due to suspension of more pollutants in the solution, turbidity and aggregation of particles lowered the effective light transmission. Thus decrease in the number of surface active sites hindered photocatalytic activity and reduced the degradation rate [44]

Effect of pH

The pH of the Congo red solution was varied from 3 to 9 and the effect of pH on the rate of photocatalytic degradation was studied while keeping other experimental conditions constant and the results are shown in Fig.12. The maximum degradation of aqueous Congo red solution was observed as 90.2% for NTZ1 and 88.2% for NTT1.5 at pH 4, and minimum as 60% for NTZ1 and 60% for NTT1.5 in average at pH 8 to 9. This is because in acidic medium titania surface remain positively charged and in basic medium negatively charged with respect to point zero charge. The anionic dyes like Congo red acts as

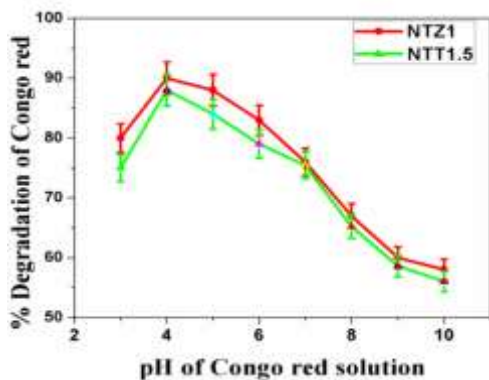


Fig.12: Effect of pH a) NTZ1 and b) NTT1.5 on the photodegradation of Congo red dye solution [Congo red = 20 μM , Amount of NTZ1&NTT1.5 =0.5 g/l, Temp [303K].

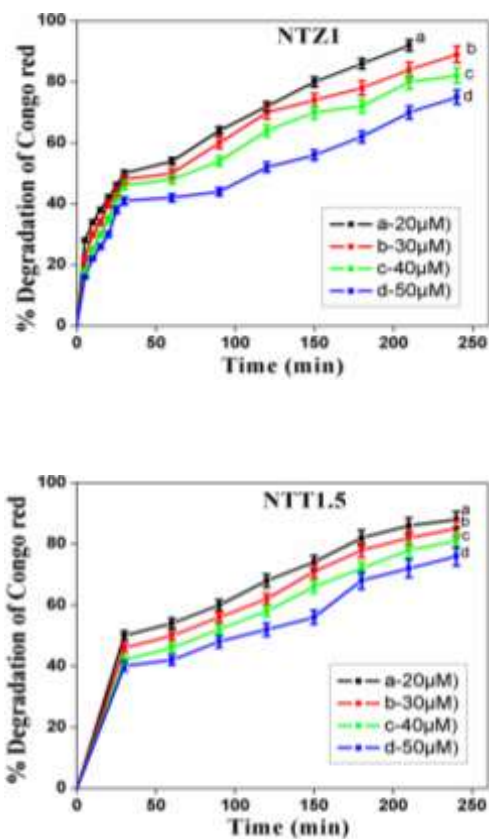


Fig. 13: Effect of Initial dye concentration of a) NTZ1 and b) NTT1.5 on the photodegradation of Congo red dye solution [pH = 4, Amount of NTZ1&NTT1.5= 0.5 g/L, Temperature=303 K].

a strong lewis base in acidic pH and get adsorbed easily on the positive titania surface [45] But in the basic medium the dye may not be adsorbed onto the negative surface of photocatalyst effectively [46], therefore decrease in the photodegradation of Congo red was observed

Effect of initial dye concentration

Fig.13 clearly indicated that the rate of photocatalytic degradation decreased with increased dye concentration and 20 μM could be chosen as the optimum dye concentration for analysis. The concentration of the Congo resolution was varied from 20 to 50 μM and all other parameters were kept constant and the study was carried out. As the concentration of the dye solution was increased more pollutants got adsorbed on the surface of TiO_2 , leading to aggregation of particles hindering the effective penetration of light [26] and therefore the number of photons reaching the catalyst surface, finally lowering the degradation percentage.

Kinetic studies

In Fig.14 it is shown that pseudo-first order reaction kinetics has been observed to describe the solid-liquid reaction for the photodegradation of Congo red. The Langmuir-Hinshelwood (L-H) kinetic expression has been used to analyze the above heterogeneous photocatalytic reaction successfully [47, 48], and the rate constant of the same was determined from the expression $\ln(C/C_0) = kt$ at a lower concentration of the Congo red. In this equation, C_0 and C represent the concentration of Congo red in the solution at time 0 and t . The first order rate constant was found to be 0.0162 and 0.158 min^{-1} with respect to NTZ1 and NTT1.5. The experimental data have been rationalized in terms of the modified form of L-H kinetic model to describe the solid-liquid reaction successfully [49]

Demineralization of Congo red by NTZ1 and NTT1.5

In Fig.15 The Total Organic Content (TOC) was determined to monitor whether the dye was only decolorized or degraded under solar irradiation. For this 100 mL of 20 μM Congo red in NTZ1 and NTT1.5 suspension was irradiated at high noon for 4h. It was found that under continuous irradiation complete decolorization was observed whereas the concentration of the carbon was decreased to about 75% and 68% of the initial concentration at the end of 240 min. This is because chromophores responsible for the characteristic colour

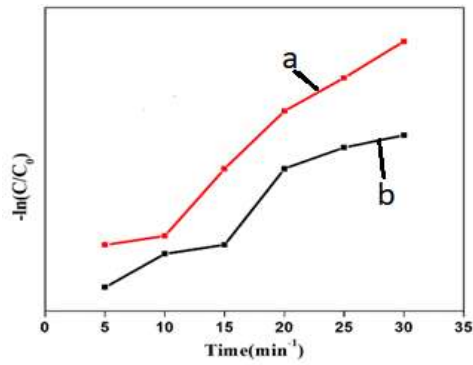


Fig.14: Kinetic study of photodegradation of Congo red by NTZ1 and NTT1.5.

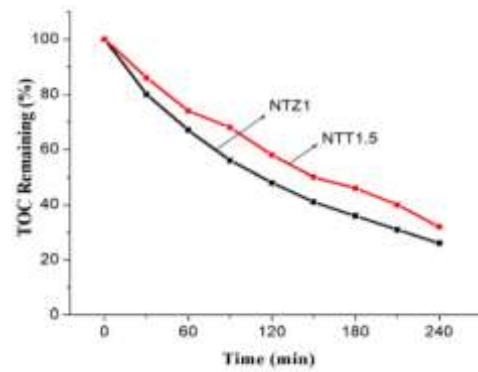


Fig.15: TOC removal efficiency of NTZ1 and NTT1.5 (Initial concentration=20µM, Catalyst dosage=0.5g/l, pH=4).

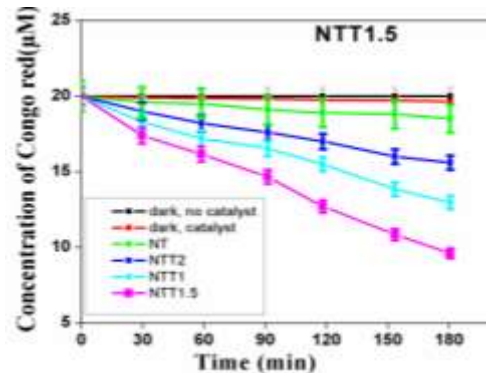
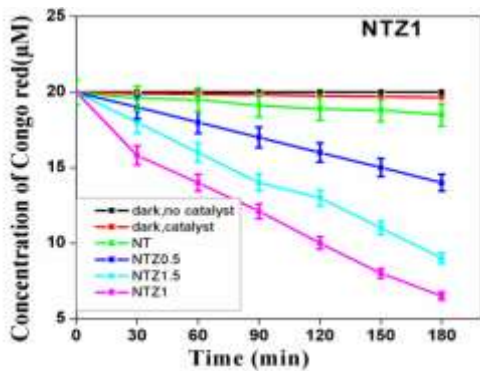


Fig.16. Degradation of Congo red by a) NTZ1 and b) NTT1.5 as photocatalysts (Initial concentration=20 µM, Catalyst dosage=0.5 g/l, pH=4).

of the Congo red was destroyed rapidly with time. But degradation which involves the breaking up of intermediate products was only partial [42]

Photodegradation of Congo red dye by NTZ1, NTT1.5, and other samples

To evaluate the efficiency of the synthesized photocatalysts, the photocatalytic degradation of Congo red dye under Sunlight has been carried out and is shown in Fig.16. About 1g/l of the catalysts were suspended in the Congo red solution of 20 µM, at pH=4, was irradiated under Sunlight. It is observed that the photocatalytic activity of NTZ1 was maximum compared to NTT1.5 and other samples. The zingiber extract-assisted nano titania catalysts showed an increase in degradation of Congo red about 10 to 30% and Tapioca extract-assisted nano titania showed 17% in comparison with nano titania synthesized without an organic extract. It is found that NTZ1 with the

surface area 60.8 m²/g, crystallite size 20.2 nm and NTT1.5 with a surface area 55.2 m²/g, crystallite size 22.6 nm have shown effective degradation under visible light supported with moderate agglomeration and reduced band gap energies. Thus high surface area, low particle size, and pure anatase phase of synthesized NTZ1 and NTT1.5 have established a marked influence of biomass on their photocatalytic activity.

The UV-Vis spectra of photodegradation of aqueous solution of Congo red in the presence of Sunlight and synthesized NTZ1 and NTT1.5 photocatalysts were examined using the Fig.17. The decrease in the absorbance as the molecules of Congo red got adsorbed on the surface of catalyst, indicated the extent of degradation [50] The spectral changes of NTZ1 and NTT1.5 obtained revealed the near completion of Congo red dye degradation within 210 and 300 min were due to effective adsorption of dye molecules on the surface [50], The disappearance and

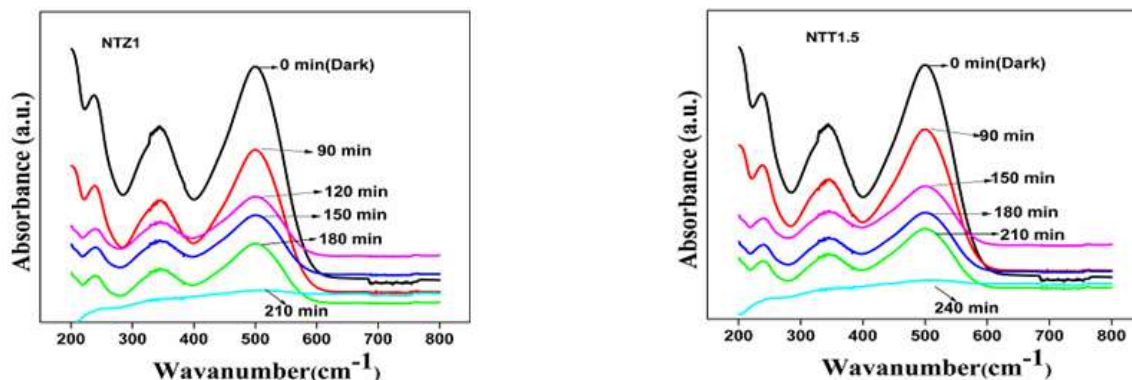


Fig.17: Absorbance spectrum of photodegradation of Congo red dye solution by NTZ1 and NTT1.5 (Initial concentration=20 μ M, Catalyst dosage=0.5 g/l, pH=4).

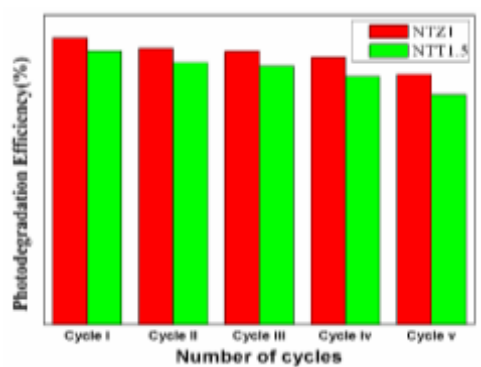


Fig.18: Recycling of photodegradation of Congo red solution using NTZ1 and NTT1.5.

lowering of absorption bands with time indicated the loss of chromophores in the visible region and the destruction of benzene and naphthalene groups in the uv region [42]

Reusability of NTZ1 and NTT1.5

The extent of recycling and reusability of NTZ and NTT1.51 was examined and is shown in Fig.18 to substantiate the utility and stability of the photocatalysts synthesized. At the end of the photocatalytic process, the catalyst was collected, filtered, washed with distilled water, and dried at 80°C in an oven. NTZ1 and NTT1.5 remained effective and reusable and have shown 94% of activity at the end of five successive cycles in the presence of solar irradiation. The marginal decrease in the recycling capacity might be due to the less number of available active species on the surface of the catalyst because of the repeated washing and the loss of catalysts.

CONCLUSIONS

Herein two novel photo active nano photocatalysts were successfully fabricated via the sol-gel technique. In this research the competent visible light photodegradation of Congo red, a textile dye taken as a model pollutant using zingiber and tapioca extracts assisted sol-gel nano titania is presented by means of comparative studies. The characterization of the samples revealed that single and mixed-phase nano catalysts produced were with reduced crystallite size, high surface area with narrow band gap required for the pronounced degradation of organic dye molecules. The various photocatalytic parameters like initial dye concentration, calcination temperature, catalyst loading, pH etc. have been optimized for achieving maximum demineralization of target material for complete abatement of water pollution. Among the synthesized photocatalysts 100 % decolorization and 0.25 μ M/minute rate of photodegradation of Congo red was reported by NTZ1, while NTT1.5 has shown 100 % and 0.21 μ M/minute. The results were highly appreciable industrially and environmentally demanding in the removal toxic contaminants from the resources in an ecosystem. For the first time, attempts have been made to exploit zingiber and tapioca extracts as templates in the synthesis of nano titania with tuned absorbance properties and to cross the benchmark of 70-74 % demineralization reported in the literature earlier. The nano photoactive catalysts synthesized in this study proved the role of the addition of simple, cost-effective, and eco-friendly templates that could serve both photodegradation and photo leaching of hazardous organic pollutants. Further the derived bio-templated nano titania

materials could be applied in biological, industrial, mechanical, and domestic waste water treatment systems.

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