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Synthesis and Characterization Of Photocatalyst for the Photodegradation Process Of Detergent for Potential Applications

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Abstract

Effective photo degradation of sewage detergents by practical application of the well known nitrogen doped titanium dioxide nanoparticle, based on green chemistry aspects of environmental renewable feedstock and design for degradation efficiency. Nitrogen doped titanium dioxide photo catalyst was synthesized using calculated quantities of titanium dioxide and urea with deionized water using drying and heating methods and the former was characterized using Energy Dispersive X - ray Analysis Ultraviolet Spectroscopy, Infrared Spectroscopy. The photo catalytic activity was analyzed by photo degradation of environmental pollutant (Sewage detergent) with different parameters under irradiation. The experiment results in an increment of degradation of the detergent by Photo catalytic activity.

Keywords: *Photodegradation, Photocatalyst, Titanium Dioxide, Urea, Detergents.*

1. Introduction

Light is very useful in chemical reactions, not only because it provides the energy needed to drive uphill processes, but also because the photogenerated molecular excited states can undergo chemical reactions that are otherwise symmetry forbidden in their ground states. Such light induced reactions come under photochemistry [1]. Domestic wastes and industrial wastes are the common well known ways as to how the water gets polluted. People fail to recognize that, the detergents used in millions of households in the world, is another way to pollute water resources and land resources. For instance, people say that waste water from the kitchen can be reused in the kitchen gardens but the outcome of the prosperity of the garden is not as prosperous as the gardens enriched with fresh water for their natural greenly growth.

In India there are mostly no proper drainage systems and most houses are built with their restroom water drainage pipes fitted to the nearest mud pile supporting trees like coconut and mango trees. Consider, the difference between a coconut tree using fresh water for growth and another tree using detergent water from the restrooms. The coconut tree using the water filled with detergents and soaps found to have weak flowers developing into weak small fruits that finally fall to the ground. In addition these trees don't grow tall and have retarded growth; the trees which were provided fresh water for its growth yielded bunch of coconuts all around the tree. These waters polluted by detergents also make the soil lose its fertility. The later reveals how this can be reduced by irradiation with urea doped Titanium Dioxide photo catalyst.

Titanium Dioxide has been a very good photocatalyst presently. One of its uses is the degradation of many pollutants of the environment. They are of high photostability, strong oxidizing power, low cost, thermal and chemical stability, resistance to photo corrosion and non-toxic in nature. For the effective utilization of ultraviolet light for absorption has a wide role of application in using Titanium Dioxide. A variety of non-metals such as N, S, C, B, and F, has been doped into Titanium Dioxide and used as photocatalysts. For the utilization of ultraviolet-visible radiation in photocatalytic reactions, nitrogen has been doped in Titanium Dioxide powders using urea. Titanium Dioxide after certain procedures becomes nitrogen doped photocatalyst which shows activity in the visible range when doped with urea [2].

Photodegradation is a process where photodegradable entities can get degraded by the photon absorption, in accordance with the wavelength of the sunlight radiations like infrared radiation, visible light radiation, and ultraviolet light radiations. Photodegradation induced by light, involves changes in the physical as well as chemical aspects of molecules caused by ultraviolet irradiation or visible light irradiation usually. Photodegradation may happen when the oxygen molecules are absent or when photooxidative degradation exists. The process of photooxidative degradation is caused by UV induced radiation with or without catalysts and can increase speed at elevated temperatures [3].

2. Review of Literature

There are varieties of findings in the research area of photocatalytic degradation. Similarities such as change in pH, photocatalytic amount has been most common in the arena. Sobczynski et al., has issued a review on "Water purification by photocatalysis on semiconductors", which covers water purification from organic matters [4].Sawadogo et al., has a issued a journal, "Effect of Detergents from Greywater on irrigation plants", which includes analyzing of pH of soil and electrical conductivity changes caused by water [5]. Legrini et al., has issued a journal, "photochemical processes for water treatment", which involves decontamination of drinking water using ozone with UV light [6]. Kishor Wani et al., has issued a journal, "Detergent Removal from Sullage by Photocatalytic process". The team has applied photocatalysis technology for the degradation of commercial detergents of washroom waste water. The Chemical Oxygen demand has been taken as a parameter for monitoring degradation rate [7]. Shivaraju et al., has issued a journal, "Removal of Organic Pollutants in the municipal sewage water by TiO_2 based heterogeneous photocatalysis", which involves evaluation of degradation efficiency through various parameters like pH, organic concentration, irradiation time [8].

3. Materials and Methods

Surf detergent, commercially available titanium dioxide powder (TiO_2), Aqueous solution of urea ($CO(NH_2)_2$), (Rankem, India) were used as supplies purchased from CDH-AR and used in the work without further purification. Nitrogen doped Titanium
Dioxide powder was used as photocatalyst. Double distilled deionizer water was obtained by distilling the distilled water over alkaline potassium permanganate used for mixing and the making of the solutions. Solvents like ethanol (99% purity), isopropanol, sodium hydroxide pellets were used for washing purposes. All reagents were used without further purification. Steam bath of about 80^oC, horizontal muffle furnace was kept at a temperature of 400 ^{o} C for 4 hours were included in heating and drying purposes. KBr (FT-IR grade), $CDCL_3$ (100atom%D), DMSO-d_6 (99.9 atom %D), D2O (99.9atom%D) (Aldrich), and mineral oil (for IR spectroscopy) (Fluka) were used as ancillaries.

Synthesis of Photocatalyst

The synthesis of nitrogen doped Titanium Dioxide photocatalyst includes the following ingredients taken in suitable proportions. Commercially available Titanium Dioxide and urea was taken in the ratio of 1:2, for the preparation of the photocatalyst [9].About 1 gram Titanium Dioxide and 2 grams of urea was dissolved with deionized water of a volume approximately of about 13 -14 ml in a borosilicate glass beaker of 100ml at room temperature [10]. The mixture was kept in dark for one day and the solution was evaporated to dryness on a steam bath being precautious that it does not get burnt or get darker in colour. The dry residue was scrapped off with a clean dry spatula and transferred to a horizontal muffle furnace and heated to 400^0 C. The sample is dried completely for 4 hours under reduced pressure to get white powdered Titanium Dioxide doped with photocatalyst. This was used for the catalytic photodegradation of detergents involved in the studies.

Experimental Procedure

The experiments were performed in a borosilicate glass of 500 ml capacity. A certain amount of surf detergent was dissolved in deionized water, filtered and centrifuged.
The concentration of this bulk centrifuged solution was taken and analyzed, mentioned as the initial value (I_0) of absorbance while taking ultraviolet spectroscopy
. The bulk centrifuged solution was distributed equally in four glass beakers (100 ml) and the resultant solutions were used for experimenting with different parameters.
These solutions were stirred under dark, dark with photocatalyst, light, and light with photocatalyst. The amount of photocatalyst usage was varied in the experiment. The solution was irradiated with artificial lamp (200 W) and solar radiation.
The Lux meter intensity of about 2500-3500 Lux was observed from the artificial lamp.
Under these parameters, the stirring detergent solution of approximate 5 ml or 10 ml, were taken out from the beaker, containing partially treated surf solution, using a dropper at a time interval of 30 minutes for 3 hours and stored for analysis.

Considering, the solution stirred under dark with catalyst and light with catalyst were collected into centrifuge tubes, centrifuged and filtered again through a filter paper and analyzed by UV-Visible Spectrometer [11].
The wavelength and absorbance values were taken for the samples kept for analyzing using the UV-Vis spectrometer and brought under investigation.
The treated detergent water can be used for irrigation and plantations as stated in the literatures.

4. Results and Discussion

Table 1: Samples experimented in the dark

time (hrs)	wavelength (nm)	absorbance **(λ)**
0	342.8 (I_0)	0.538
0.5		0.548
1		0.544
1.5		0.542
2		0.539
2.5		0.535
3		0.539

Table 2: Samples experimented in the dark with photocatalyst

time (hrs)	wavelength (nm)	absorbance **(λ)**
0	342.8 (I_0)	0.538
0.5		0.535
1		0.45
1.5		0.42
2		0.39
2.5		0.313
3		0.29

Table 3: Samples experimented in the light alone

time (hrs)	wavelength (nm)	absorbance **(λ)**
0	342.8 (I_0)	0.538
0.5		0.53
1		0.524
1.5		0.511
2		0.486
2.5		0.419
3		0.398

Table 4: Samples experimented in the light with photocatalyst

time (hrs)	wavelength (nm)	absorbance (λ)
0	342.8 (I_0)	0.538
0.5		0.04
1		0.039
1.5		0.036
2		0.032
2.5		0.03
3		0.021

Table 5: Comparison of the variations in catalytic quantities

time (hrs)	wavelength (nm)	absorbance of sample using catalyst (5 mg)	absorbance of sample using catalyst (10 mg)
0	342.8 (I_0)	0.538	0.538
0.5		0.301	0.04
1		0.215	0.039
1.5		0.156	0.036
2		0.115	0.032
2.5		0.088	0.03
3		0.056	0.021

Table 6: Samples experimented in solar light

time (hrs)	wavelength (nm)	absorbance **(λ)**
0	342.8 (I_0)	0.538
0.5		0.492
1		0.48
1.5		0.456
2		0.291
2.5		0.183
3		0.158

Degradation of the pollutant material (Detergent) applied with solar light at an initial wavelength of 335.6nm and 10 mg of the photocatalyst and its efficiency of degradation are shown above.

Table 7: Determination of the pH level

Before degradation of the detergent	10.36 pH
After degradation of the detergent	9.30 pH

It is observed that there has been a reduction in pH level after the degradation process of detergent containing water.

Representation of the graph of samples experimented with different parameters

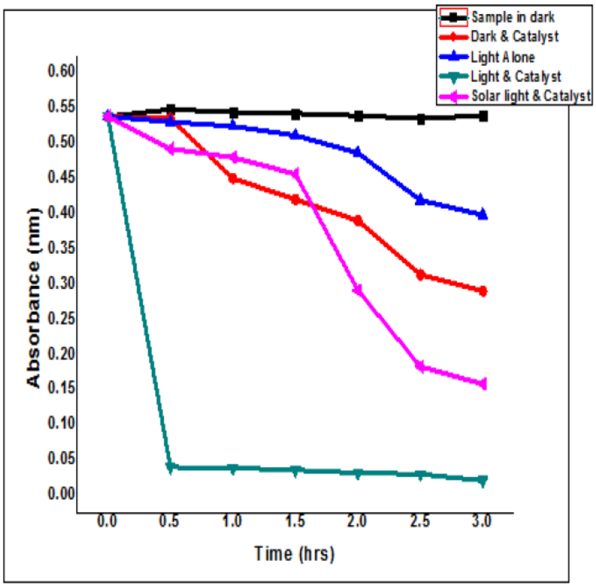

Fig. 1 Representation of the graph of the samples experimented with different parameters such as, samples experimented in the dark, sample experimented in the dark with catalyst and sample experimented with light alone and sample experimented with light with catalyst. The readings reveals their degradation efficiency one after other, concluding that the samples with treated detergent using nitrogen doped titanium dioxide photocatalyst shows increased degradation efficiency than others.

Comparison of the samples treated with varying amount of photocatalytic quantity

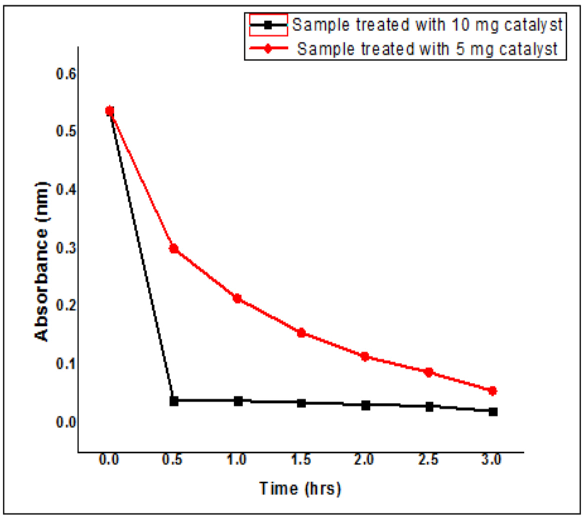

Fig. 2 Representation of the graph of the detergent samples treated with 10 mg and 5mg photocatalyst, which shows the efficiency in degradation of the pollutants while using the N-TiO_2 photocatalyst.

Energy Dispersive X-Rays Analysis (Edax) of the Nitrogen Doped with Titanium Dioxide as Photocatalyst

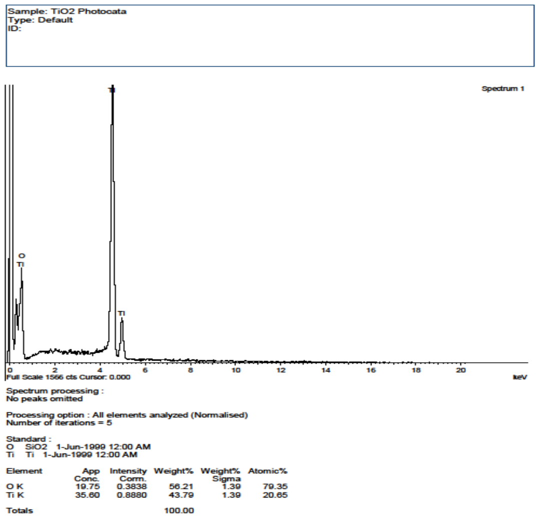

Fig. 3 Energy dispersive spectroscopy is a high quality data processed, displayed graphically, for giving accurate results.

This gives the chemical element composition of the samples. Energy dispersive spectrum for the samples was taken; using Oxford instrument UK, having the model INCA Energy 250 LN2 Closed. Data acquisition can be obtained from this.

Infrared characterization of the nitrogen doped TiO_2 as photocatalyst

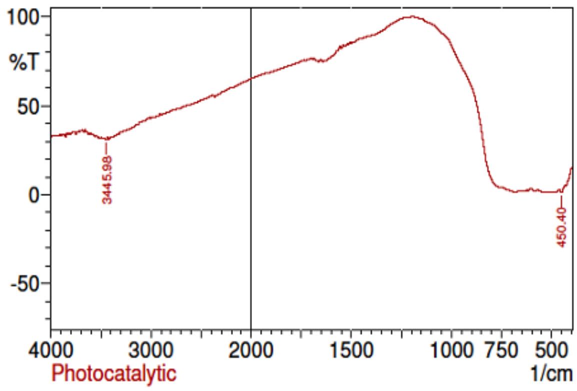

Fig. 4 IR Spectrum of nitrogen doped with TiO_2 as photocatalyst

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Table 8: IR Characterization intensity data

	Peak	Intensity	Correction Intensity
1	450.4	1.621	2.43
2	3445.98	30.863	1.209

Table 9: IR Characterization base area correction data

Base (H)	Base (L)	Area	Correction Area
463.9	433.04	48.359	5.288
3466.23	3432.48	17.017	0.337

Infrared spectrum for the samples was recorded on a FT - IR Spectrometer model, Shimadzu Spectrum RX- I ranging 4000 - 400 cm-1. Transparent KBr pellets were made for taking spectra of the solid samples. Samples that are of liquid forms can be recorded using Nujol mulls, Fluka; including the KBr windows usage.

The IR spectrum of the nitrogen doped Titanium Dioxide photocatalyst shows broad band in the region 3445.98cm^{1}, indicating the O-H stretching vibration and the absorption band in the range of about 1600 cm^{-1}, indicates O-H bending vibration modes of water adsorbed in the oxide surface; further broadening of absorption band indicates the Ti-O stretching frequencies [12].

Ultraviolet characterization of Nitrogen doped Titanium Dioxide Photocatalyst

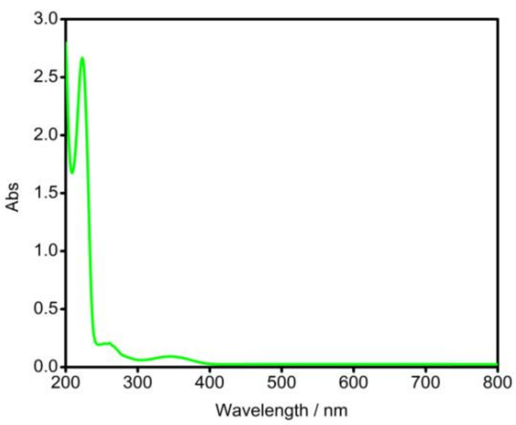

Fig. 5 UV spectra of doped TiO_2 with nitrogen as photocatalyst are seen above.

The ultraviolet spectrum gives an absorption band at 311 nm with an absorbance of about 0.348cm^{-1}. The electronic absorption spectrum for the samples was received on a Double Beam Spectrophotometer 2203, Systronics, transferred to the computer through suitable double beam spectrometer software. The spectra ranging 200-800 nm with cuvette stoppered with Teflon of 1cm length.

Scanning Electron Microscope analysis of the Nitrogen doped Titanium Dioxide photocatalyst

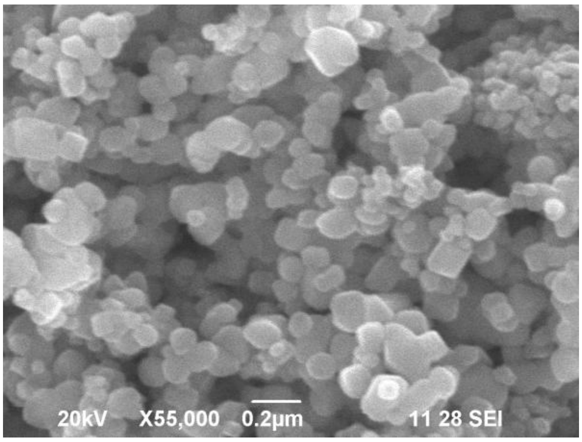

Fig. 6 **R**epresents SEM image of doped Titanium Dioxide using nitrogen as photocatalyst.

The SEM image of the doped Titanium Dioxide using nitrogen photocatalyst is exposed at X55, 000 pixel resolution at nanoscale level.. SEM image for the sample was recorded, by JEOL Ltd from Japan using the model JSM 6390.

X-Ray Diffraction Analysis for Nitrogen Doped Titanium Dioxide Photocatalyst

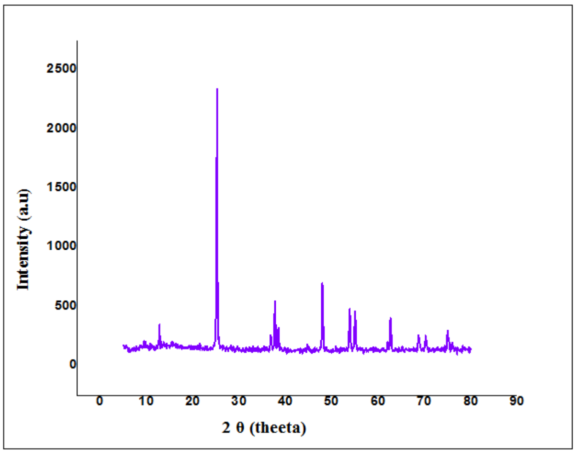

Fig. 8 Represents X-Ray Diffraction analysis of doped Titanium Dioxide using nitrogen photocatalyst.

Table 10: XRD Characterization data of photocatalyst

Strongest peaks	2 θ (deg)	d (A)	FWHM (deg)	Intensity (counts)	Integrated Intensity counts
1	25.1606	3.5366	0.2749	907	2265
2	47.918	1.8969	0.2893	293	931
3	37.6669	2.3862	0.2939	184	609

XRD for the photocatalyst has been recorded by the instrument model XRD- 6000, Shimadzu, Japan.

5. Conclusion

A mild and efficient way for the treatment and reduction of impurities in polluted water was applied. Efficiency of degradation process with various conditions was specified. Demonstration using plantations were implied. Synthesized compounds were characterized using, pH meter, Energy dispersive spectrum using X-rays, Ultraviolet Spectroscopy, Infrared Spectroscopy, observation of electron beam scanning pattern of X-ray diffractions. The future scope can be by varying dopants of the catalyst and usage in various degradation process.

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