Activated Carbon Loaded N, S co-doped TiO₂ Nanomaterial and Its Dye Wastewater Treatment

J. Kamalakkannan, V. L. Chandraboss, S. Prabha, S. Senthilvelan*

Department of Chemistry, Annamalai University, Annamalainagar 608 002.India

*E-mail address: dr_senthilvel@yahoo.co.in

ABSTRACT

Activated carbon (AC) loaded nitrogen and sulfur (N, S) co-doped TiO₂ nanomaterial (AC-N-S-TiO₂) was prepared by precipitation method. AC-N-S-TiO₂ material was characterized by Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray analysis (EDX), X-ray diffraction (XRD), Fourier Transform - Infrared (FT-IR), Photoluminescence (PL) and atomic force microscopy (AFM) analysis. Photodegradation and decolorization of Malachite green (MAG) and Methyl green (MEG) by using TiO₂, N-S-TiO₂ and AC-N-S-TiO₂ under UV-light irradiation has been carried out. The photocatalytic activity of the AC-N-S-TiO₂ was higher than that of the undoped and N, S-doped TiO₂. The hydroxyl radical analysis - Fluorescence technique with coumarin has been discussed. The photodegradation of MEG was well described by analyzed to be pseudo-first order according to the Langmuir-Hinshelwood representation, the high quantum yield set up to be calculated, stability and reusability of nanomaterial. AC-N-S-TiO₂ act as a promising photocatalyst for dye wastewater treatment under UV-light irradiation.

Keywords: Activated carbon; Nanomaterial; Photocatalysis; Malachite green; Methyl green; UV-light

1. INTRODUCTION

Metal oxides are the mainly excellent choice for the heterogeneous photocatalysis to eliminate various pollutants and hazardous dyes [1-3]. The use of TiO₂ as a semiconductor photocatalyst is an efficient method for elimination of environmental pollutants especially for the degradation of organic contaminants from water has been reported and researched under various contexts [4].

TiO₂ is one of the important semiconductor photocatalyst for the degradation of pollutants due to its biological and chemical inertness, great photoreactivity, non-toxicity and photostability [5-7]. Doping different elements into TiO₂, including metal [8, 9] and non-metal elements increases the photocatalytic efficiency [10, 11]. Researchers indicated that N-containing [12] S-containing [13] or N-doping [14, 15] S-doping [16] and N, S co-doping of TiO₂ can improve the visible light response [7].

Malachite green (MAG) is an extensively used biocide dye in worldwide aquaculture production. It is also used as a medical disinfectant, food colouring agent, food additive and anthelmintic. However, MAG has now become a highly controversial compound due to the

associated risks in reproductive system, immune system, carcinogenic and genotoxic properties [17]. Methyl green (MEG) is used extensively in the fabric industry for dyeing nylon, silk, wool and cotton as well as for colouring of oil, waxes, fats and varnish [18]. The binding of MEG to DNA is possibly ionic, as opposed to intercalative, and it remains so stably bound to double-stranded DNA that, with its modification to the colorless carbinol form, it has been used to evaluate the binding of other molecules to DNA [19, 20].

Activated carbon (AC) is having greater adsorption property; it does not degrade the dye.

But AC loaded on semiconductor oxide improves the degradation efficiency of semiconductor oxide by its synergetic effect. The increase in photocatalytic activity of semiconductor oxide by the loading of AC has been well established [21-23]. This phenomena having promising solution to the water purification technology.

In this work, we report the synthesis, characterization and photocatalytic activity of AC-N-S-TiO₂ nanomaterial. The obtained material was characterized by SEM with EDX, XRD, FT-IR, PL and AFM analysis. Photocatalytic activity of this material towards MAG and MEG in aqueous solution under UV-light irradiation was studied. AC-N-S-TiO₂ reveals enhanced photocatalytic activity when compared to TiO₂ and N-S-TiO₂ on the degradation and decolorization of MAG and MEG dyes under UV-light irradiation.

2. EXPERIMENTAL SECTION

2.1. Materials

Tetra isopropyl orthotitanate (C₁₂H₂₈O₄Ti), activated carbon, ammonium sulphate ((NH₄)₂SO₄), nitric acid (HNO₃), malachite green (C₂₃H₂₅ClN₂), methyl green (C₂₆H₃₃N₃Cl₂) and ethanol (C₂H₅OH) were the guaranteed reagents of Sigma Aldrich and used as such. The aqueous solutions were prepared by using double distilled water. Chemical structure of MAG and MEG is shown in Fig. 1.

Fig.1. Chemical structure of (a) malachite green and (b) methyl green.

2.2. Synthesis of AC-loaded N, S co-doped TiO₂ nanomaterial

AC-N-S-TiO₂ material was synthesized by the precipitation method (Scheme 1). Briefly, a constant amount of ammonium sulphate was dissolved in anhydrous ethanol. The resulting solution was added dropwise into tetra isopropyl orthotitanate in ethanol solution at room temperature, further 0.1M charcoal was added to the above solution under vigorous stirring for 6 h than 2-3 drops of conc. nitric acid were added. The obtained solution was stirred for 1 h than ultra-sonication for 40 min, until precipitate formed. The obtained precipitate was washed with water and ethanol. Then the precipitate was collected and dried in oven at 100 °C for 8 h in air. The resulting material was finally calcined at 300 °C for 2 h, to obtain AC-N-S-TiO₂ nanomaterial.

Scheme 1. Schematic representation for the synthesis of AC-N-S-TiO₂ nanomaterial.

2.3. Photocatalysis

The photocatalytic activities of the photocatalysts (TiO₂, N-S-TiO₂ and AC-N-S-TiO₂) were evaluated by the photodegradation of MAG and MEG. The light source was a UV lamp (365 nm). The reaction was maintained at ambient temperature (303 K). In a typical experiment, aqueous suspensions of dye (50 mL, 1×10⁻⁴ M) and 0.16 g of the photocatalyst powder were placed in reaction tubes. Prior to irradiation, the suspension was magnetically stirred in the dark to ensure the establishment of an adsorption/desorption equilibrium. The suspension was kept under constant air-equilibrated condition. At the intervals of given irradiation time. The suspension was measured spectrophotometrically MAG (614 nm) and MEG (630 nm) within the Beer–Lambert law limit.

2.4. Characterization methods

X-ray diffraction (XRD) spectra was recorded on the X'PERT PRO model X-ray diffractometer from Pan Analytical instruments operated at a voltage of 40 kV and a current of 30 mA with Cu K α radiation.

Scanning electron microscopy (SEM) with elementary dispersive X-ray analysis (EDX) was carried out on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25 °C. The sample was prepared by placing a small quantity of prepared material on a carbon coated copper grid and allowing the solvent to evaporate.

Fourier transform-infrared spectrum (FT-IR) was recorded using SHIMADZU FT-IR spectrometer in KBr pellet.

Photoluminescence (PL) spectra at room temperature were recorded using a Perkin-Elmer LS 55 fluorescence spectrometer. Nanoparticles were dispersed in chloroform and excited using light of wavelength 300 nm.

Atomic force microscopic (AFM) image was taken by using AGILENT-N9410A series 5500 microscope operating in the tapping mode with standard silicon nitride tips. This instrument uses a silicon nitride tip a radius of 20 nm and a low resonance frequency cantilever that has a manufactures spring, constant at 30-45 nm. Scan of 5 x 5 μ m obtained for sample. The images were recorded in condition to produce 2D and 3D images.

Ultraviolet and visible (UV-vis) absorbance spectra were measured over a range of 800-200 nm with a Shimadzu UV-1650PC recording spectrometer using a quartz cell with 10 mm of optical path length.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

The obtained XRD of the TiO₂ and AC-N-S-TiO₂ nanomaterial is shown in Fig. 2a and 2b respectively. The peaks at 25.47°, 31.60°, 37.54°, 43.48°, 47.78°, 54.73° and 62.41° are the diffractions of the TiO₂ (101), (101), (004), (111), (200), (211) and (204) crystal planes and materials to anatase phase (JCPDS No. 21-1272). But, AC-N-S-TiO₂ XRD peaks are slightly shifted from the anatase TiO₂ as 25.12°, 32.12°, 37.97°, 42.17°, 47.87°, 54.72° and 61.02° are indexed as the TiO₂ (101), (101), (004), (111), (200), (211) and (204) crystal planes. It has no XRD peaks related to the dopants (Nitrogen and Sulfur) and loaded Carbon. It is due to the less concentration of the dopants and loading.

The average crystalline size (L) of the AC-N-S-TiO₂ material can be calculated from the Debye-Scherrer formula [24]. $L = 0.89\lambda / \beta \cos\theta$ where L is the crystalline size (in nm), λ is the wavelength (in nm), β is the full width at half maximum intensity (FWHM-in radian), and θ is the Bragg diffraction angle (°). The average crystalline size of the AC-N-S-TiO₂ synthesized was figured out to be about 38 nm.

Fig.2. XRD patterns of (a) undoped TiO_2 and (b) AC-N-S- TiO_2 nanomaterial.

3.2. SEM with EDX analysis

The surface morphology and elemental studies of the TiO_2 , N-S- TiO_2 and AC-N-S- TiO_2 nanomaterial were carried out using SEM with EDX analysis (Figs. 3 and 4). The SEM images revealed that individual nano aggregates particle were composed by a collection of elongated particles of various size and shapes. The elongated shape of the AC-N-S- TiO_2 material revealed by SEM is in perfect agreement with the results observed by XRD (Fig. 2). AC-N-S- TiO_2 shows the average particle size of 38 nm (Fig. 3c). EDX analysis confirms Titanium and Oxygen are present in pure TiO_2 (Fig. 4a), Nitrogen, Sulfur, Titanium and oxygen are present in N-S- TiO_2 material (Fig. 4b), where as Carbon, Nitrogen, Sulfur, Titanium and oxygen are present in AC-N-S- TiO_2 nanomaterial (Fig. 4c).

Fig.3. SEM images of (a) undoped TiO_2 , (b) N-S-TiO_2 and (c) AC-N-S-TiO_2 nanomaterial.

Fig.4. EDX analysis of (a) undoped TiO_2 , (b) N-S-TiO_2 and (c) AC-N-S-TiO_2 nanomaterial.

3.3. FT-IR analysis

The FT-IR spectra of the TiO_2 , N,S- TiO_2 and AC-N-S- TiO_2 materials were shown in Fig. 5. The IR spectrum of the Fig. 5a shows the absorption peak at $3370\text{--}3525\text{ cm}^{-1}$ and 1635 cm^{-1} corresponding to stretching vibrations of the -OH and bending vibrations of the adsorbed water molecules respectively. The main absorption peaks at 482 and 671 cm^{-1} was assigned to the Ti-O and Ti-O-Ti bonds. Fig. 5b shows the absorption peak at $3300\text{--}3550\text{ cm}^{-1}$ was assigned to the stretching vibration of surface -OH group. The main absorption peaks at 1625 cm^{-1} was assigned to the stretching vibration of N-H group. Ti-O-N and Ti-O-S bonds of the sample emerged at 1134 and 1047 cm^{-1} respectively. Fig. 5c shows the absorption peak at 3174 cm^{-1} and assigned to the stretching vibration of surface -OH group. The main absorption peaks at 1625 cm^{-1} was assigned to the stretching vibration of N-H group. Ti-O-N, Ti-O-S and Ti-O-C bonds of the sample emerged at 1134 , 1047 and 1035 cm^{-1} [25].

Fig.5. FT-IR spectrum of a) TiO_2 , b) N, S- TiO_2 and c) AC-N-S- TiO_2 nanomaterial.

3.4. PL analysis

Photoluminescence spectra of TiO_2 , N-S- TiO_2 and AC-N-S- TiO_2 are shown in Fig. 6a, 6b and 6c respectively. As the photoluminescence occurs due to electron–hole recombination, its intensity is directly proportional to the rate of electron–hole recombination [26]. TiO_2 gave six emissions at 363, 402, 437, 487, 531, and 595 nm. N-S- TiO_2 gave five emissions at 363, 398, 439, 485 and 531 nm and AC-N-S- TiO_2 gave five emissions at 363, 398, 438, 487 and 531 nm. In N, S- TiO_2 and AC-N, S- TiO_2 slightly shift in emission compared to the undoped TiO_2 material was observed. The intensity of AC-N-S- TiO_2 emission is less when compared to that of TiO_2 and N-S- TiO_2 materials. This is because of suppression off recombination of electron–hole pairs by AC-N-S- TiO_2

Fig.6. PL spectra of (a) undoped TiO_2 , (b) N-S- TiO_2 and (c) AC-N-S- TiO_2 nanomaterial.

3.5. AFM analysis

The morphology of the synthesized AC-N-S- TiO_2 nanomaterial has been studied by AFM. Fig. 7a depicts typical AFM image of AC-N-S- TiO_2 . The corresponding cross-sectional view indicates that the average thickness of AC-N-S- TiO_2 is about 32.5 nm. (Fig. 7b). The existence of nanosized particles in the AC-N-S- TiO_2 is more clearly reflected in three-dimensional (3D) AFM image. This image shown wave type projection in the Z direction from the fine surface and smaller size of AC-N-S- TiO_2 was clearly noticed. Thus the above results confirm the nano texture in the surface of as-synthesized AC-N-S- TiO_2 material.

Fig.7. (a) AFM image ($5 \times 5 \mu\text{m}$) of as synthesized AC-N-S-TiO₂ nanomaterial, with scale bars at 0-32.5 nm and (b) Three-dimensional (3D) AFM image of surface micelles of AC-N-S-TiO₂ nanomaterial ($5 \mu\text{m} \times 5 \mu\text{m} \times 32 \text{ nm}$).

3.6. Photodegradation and decolorization of MAG and MEG under UV-light irradiation

We have chosen photodegradation and decolorization of MAG and MEG dyes under UV light irradiation to evaluate the photocatalytic activity of the proposed photocatalyst. Figs. 8 and 9 show the time course of decrease in the absorbance of MAG and MEG under UV light irradiation. The photodegradation process of MAG, the UV-vis spectra and the colours of MAG aqueous solution as a function of UV-light irradiation time in the presence of photocatalysts (TiO₂, N-S-TiO₂ and AC-N-S-TiO₂) are illustrated in Fig 8a, 8b and 8c. The photodegradation process of MEG, the UV-vis spectra and the colours of MEG aqueous solution as a function of UV-light irradiation time in the presence of photocatalysts (TiO₂, N-S-TiO₂ and AC-N-S-TiO₂) are illustrated in Fig. 9a, 9b and 9c. It can be seen from UV-visible spectra changes, the strong adsorption peak of MAG and MEG solutions at 614 nm and 630 nm steadily decreased with increasing the light irradiation time. AC-N-S-TiO₂ exhibited excellent photocatalytic activity for MAG and MEG under UV-light irradiation when compared to that of TiO₂ and N-S-TiO₂ nanomaterials.

Fig. 10 shows the time course of percentage degradation of MAG (Fig. 10a) and MEG (Fig. 10b) under UV-light irradiation. After 75 min irradiation time AC-N-S-TiO₂ degrade MAG aqueous solution up to 52.8% compared to that of TiO₂ and N-S-TiO₂ (42.6 % and 46.8 %). After 60 min irradiation time AC-N-S-TiO₂ can degrade the MEG aqueous solution up to 56.1 % compared to that of TiO₂ and N-S-TiO₂ (45.9 % and 38.2 %).

Fig. 11 shows the time course of percentage decolourization of MAG (Fig. 11a) and MEG (Fig. 11b) under UV-light irradiation. After 75 min of irradiation time AC-N-S-TiO₂

decolourize the MAG in aqueous solution up to 93.04 %. But TiO_2 and N-S- TiO_2 (73.4 % and 78.8 %) decolorize only respectively. After 60 min of irradiation time AC-N-S- TiO_2 decolorize the MEG aqueous solution up to 92.87 %. But TiO_2 and N-S- TiO_2 decolorize (60.9 % and 90 %). Photodegradation and decolourization of MAG and MEG in dark and in absence of the catalyst does not significant. Thus AC-N-S- TiO_2 exhibited higher photocatalytic activity when compared to that of TiO_2 and N-S- TiO_2 photocatalysts.

Fig.8. Absorption spectra changes of MAG (1×10^{-4} M, 50 mL) in the presence of photocatalysts (a) undoped TiO_2 , (b) N-S- TiO_2 and (c) AC-N-S- TiO_2 under UV-light (365 nm) irradiation at 15 minutes interval, photocatalytic activity for the degradation of MAG by AC-N-S- TiO_2 nanomaterial.

Fig.9. Absorption spectra changes of MEG (1×10^{-4} M, 50 mL) in the presence of photocatalysts (a) undoped TiO_2 , (b) N-S- TiO_2 and (c) AC-N-S- TiO_2 under UV-light (365 nm) irradiation at 15 minutes interval, photocatalytic activity for the degradation of MEG by AC-N-S- TiO_2 nanomaterial.

Fig.10. Comparison of photocatalytic activity (degradation (%) vs time (min)) of degradation of (a) MAG and (b) MEG by using TiO_2 , N,S-TiO_2 and AC-N,S-TiO_2 under UV-light (365 nm) irradiation at 15 minute interval.

Fig.11. Comparison of photocatalytic activity (decolourization (%) vs time (min)) of decolourization of (a) MAG and (b) MEG by TiO_2 , N,S-TiO_2 and AC-N,S-TiO_2 nanomaterial under UV-light (365 nm) irradiation at 15 minute interval.

3.7. Different catalyst loading and Different concentration of MEG dye

The effect of catalyst loading AC-N,S-TiO_2 on MEG has been fast degradation carried out in the range of 0.100g, 0.160g and 0.250g the total volume of solution to uses 50

mL. The various amount of catalyst loading in the reaction medium of degradation rate. The rate is linearly related to the amount of catalyst loadings. Among the catalysts in the AC-N-S-TiO₂ (0.200g) showed higher activity when compared to low catalyst loading (0.100g) shows in Fig. 12a. The effect of various dye concentration of MEG on AC-N-S-TiO₂ under UV light represents. Different concentrations of (1×10^{-4} and 1×10^{-5}) MEG the increase of illumination with material were prepared and it was used for the photodegradation process by using UV light. Photodegradation of MEG was higher in lower concentration when compared to of it higher concentration shows in Fig. 12b.

Fig.12(a). Different catalyst loading AC-N-S-T (0.100g, 0.160g and 0.200g) +MEG (1×10^{-4})
(b) Different concentration of MEG dye (1×10^{-4} and 1×10^{-5}).

3.8. Reusability of the catalyst

The reusability of AC-N-S-TiO₂ was tested for the degradation of dyes MEG and MAG under identical reaction conditions. After full degradation, the catalyst was alienated and washed with a bulky amount of deionized water. The improved catalyst was dried in a hot air oven at 100 °C for 90 min and used for a second run. Figure 13 shows the results of MEG degradation for fifth runs. AC-N-S-T exhibits amazing photostability as the MEG and MAG degradation percentages are 100, 98, 97, 97 and 97% and 100, 98, 97, 95 and 95 for 75 min in the 1st, 2nd, 3^d, 4th, and 5th runs, respectively. There is no significant change of reused AC-N-S-TiO₂ photocatalyst did not change during the reaction, representing the stability of photocatalyst. After conclusion of the degradation reaction, the solution was tested for Ti³⁺ leaching with sodium sulfide. There is no precipitation of titanium sulfide (black color)[27]. As there is no leaching of Ti³⁺, this catalyst is non-hazardous for wastewater behavior.

Fig.13. Reusability of the catalyst.

3.9. Data analysis

3.9.1. Degradation of kinetic study

A solution of (1×10^{-4}) MEG was prepared in doubly distilled water and 0.160 g of catalyst was loaded to it. It was observed that there was a decrease in absorbance of MEG solution with increasing time of revelation of UV light. A linear plot between $1 + \log A$ Vs time was obtained, which indicates that the photocatalytic degradation of MEG follows pseudo-first order kinetics. The rate constant for this reaction was measured with the facilitate of following equation [28]

$$k = 2.303 \times \text{slope} \quad (1)$$

Prepared nanomaterial for TiO_2 and AC-N-S- TiO_2 degradation rate calculation in precence of the rate is linearly related to the amount of catalysts. Between the two catalysts only doped showed higher the rate when compared to undoped nanomaterial. (Fig. 14).

Fig.14. Data analysis C/C_0 .

3.9.2. Quantum yield

The quantum yield of a photocatalytic reaction is defined as the number of MEG dye molecules individual decaying (degraded) per photon absorbed (eq 2).

$$\Phi = \text{Number of molecules decaying} / \text{Number of photons of light absorbed} \quad (2)$$

The photodegradation rate constants (k') of MEG dye under the monochromatic light source can also be used for calculation of its reaction quantum yield [29] using eq. 3

$$\Phi = \frac{k}{2.303 I_{0,\lambda} \epsilon_{D\lambda} l} \quad (3)$$

where Φ is quantum yield (dimensionless), I_0 is the light intensity of the occurrence light range at 200–800 nm range (1.381×10^{-6}), $\epsilon_{D\lambda}$ is the molar absorptivity of MEG at 630 nm ($1.0 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$), and l is the path length (1 cm) of the reaction and is for 50 mL of irradiation solution. The consequences of degradation quantum yields by, un doped TiO_2 and AC-N-S- TiO_2 are 0.06703 and 0.5478 mole/Einstein [30], respectively. These results indicate that the quantum yield of the AC-N-S- TiO_2 process is high when compared to other processes.

3.9.3. Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation methyle green dye is future as follows:

Methyl green absorbs radiations of preferred wavelength and it is excited giving its first excited. Singletstate. more, it undergoes intersystem crossing (ISC) to give its other stable triplet state. Along with this, the semiconducting AC-N-S - TiO_2 (SC) also utilizes this energy to motivate its electron from valence band to the conduction band. An electron can be abstracted from hydroxyl ion by hole (h^+) present in the valence band of semiconductor generate $\cdot \text{OH}$ radical. This hydroxyl radical willpower oxidizes methyl green to its leuco form, which may finally degrade to products. It was specific that the $\cdot \text{OH}$ radical participates as an active oxidizing

species in the degradation of methyl green as the rate of degradation was significantly reduced in presence of hydroxyl radical searcher (2-propanol)[28].

3.9.4. OH radical analysis

Definite by the detection of $\cdot\text{OH}$ shows the changes of the fluorescence spectra of coumarin solution in UV-light irradiation as a role of irradiation time (AC-N-S-TiO₂ - 30 and 60 min). This result suggests that the fluorescence intensity arises [31]. The emission spectra excited at 320 nm in coumarin solution added with AC-N-S-TiO₂ samples were measured Fig. 15 Displays that fluorescence signal at 391.5 nm for different time of addition with AC-N-S-TiO₂ samples. The highest fluorescence intensity was found for AC-N-S-TiO₂ at 60 min. This suggests that the fluorescence is caused by chemical reactions of coumarin with hydroxyl radicals created in photocatalytic reactions [32]. Moreover at 60 mins AC-N-S-TiO₂ sample with maximal photocatalytic activity produced much more reactive hydroxyl radicals than other samples, which is also consistent with the results of photocatalytic decay. The hydroxyl radical analysis further Definite that the hydroxyl radicals are active species using photocatalytic reactions. On the other hand, the arrangement rate of $\cdot\text{OH}$ is directly linked to the photocatalytic activity of AC-N-S-TiO₂ nanomaterial.

Fig.15. Fluorescence spectra measured at $\lambda_{\text{max}} = 320$ nm for the AC-N-S-TiO₂ samples obtained using various time (30 and 60 min) in coumarin solution (sample was illuminated for 60 min of UV light).

4. CONCLUSIONS

AC-N-S-TiO₂ nanomaterial was synthesized by precipitation method. This material was characterized by XRD, SEM with EDX, FT-IR, PL and AFM analysis. XRD, SEM and AFM analysis of AC-N-S-TiO₂ showed the average particle size of as 38 nm. FT-IR and EDX shows the C, N, S, Ti and O present in the AC-N-S-TiO₂ material. The intensity of AC-N-S-TiO₂ PL emission is less when compared to that of TiO₂ and N-S-TiO₂ materials, due to the suppression of recombination of electron-hole pairs by AC-N-S-TiO₂. The photocatalytic activity of the AC-N-S-TiO₂ material is higher than that of the TiO₂ and N-S-TiO₂ materials. The mechanism of photocatalytic defnids of MEG is due to formation of hydroxyl radical analysis. The OH radical analysis further confirms that the OH radicals are active species in the photocatalytic reactions. The formation rate of OH radicals is directly related to the photocatalytic activity of AC-N-S-TiO₂. nanomaterial, indicated which was confirmed by the Fluorescence analysis. That the photocatalysis process in the presence of AC-N-S-TiO₂, obtainable the maximum quantum yield, It is act as a promising photocatalyst for removal of dye containing wastewater behavior under UV-light irradiation.

Conflict of Interest

The authors declare no competing financial interest.

References

- [1] Liu, R.; Wang, P.; Wang, X.; Yu, H.; Yu, J., *J. Phys. Chem., C* 2012, 116, 17721–17728.
- [2] Chandraboss, V.L.; Natanapatham, L.; Karthikeyan, B.; Kamalakkannan, J.; Prabha, S.; Senthilvelan, S., *Res. Bull.* 2013, 48, 3707–3712.
- [3] Chandraboss, V.L.; Senthilvelan, S.; Natanapatham, N.; Murugavelu, M.; Loganathan, B.; Karthikeyan, B. *J. Non-Cryst. Solids.*, 2013, 368, 23-28.
- [4] Shon, H.K.; Phuntsho, S.; Vigneswaran, S, Desalin. *Water Treat.*, 2008, 225, 235–248.
- [5] Rauf, M.A.; Meetani, M.A.; Hisaindee, S, Desalin. *Water Treat.*, 2011, 276, 13-27.
- [6] Zhao, B.; G. Mele, G.; Pio, I.L.I.; L. Palmisano, L.; Vasapollo, G, *J. Hazard. Mater.*, 2010, 176, 569-574.
- [7] Rengifo-Herrera, J.A. Pulgarin, C, *Sol. Energy.*, 2010, 84, 37-43.
- [8] Dvoranova, D.; Brezova, V.; M. Mazur, M.; Malati, M.A, *Appl. Catal. B: Environ.*, 2002, 37, 91–105.
- [9] Li, X.Y.; Yue, P.L.; Kutal, C, *New J. Chem.*, 2003, 27, 1264–1269.
- [10] Khan, S.U.M.; Al-Shahry, M.; Ingler, W. B., 2002, 297, 2243–2245.

-
- [11] Yu, J.C.; Yu, J.; Ho, J.; Jiang, Z.; Zhang, L. Effects of F⁻ doping on the photocatalytic activity and microstructures of nanocrystalline TiO₂ powders. *Chem. Mater.* 2002, 14, 3808–3816.
- [12] Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*. 2001, 293, 269–271.
- [13] Yang, X.X.; Cao, C.D.; Erickson, L.; Hohn, K.; Maghirang, R.; Klabunde, K. Photocatalytic degradation of Rhodamine B on C-, S-, N-, and Fe-doped TiO₂ under visible-light irradiation. *Appl. Catal. B: Environ.* 2009, 91, 657–662.
- [14] Ma, Y.F.; Zhang, J.L.; Tian, B.Z.; Chen, F.; Wang, L.Z. Synthesis and characterization of thermally stable Sm, N co-doped TiO₂ with highly visible light activity. *J. Hazard. Mater.* 2010, 182, 386–393.
- [15] Kuo, Y.L.; Su, T.L.; Kung, F.C.; Wu, T.J. A study of parameter setting and characterization of visible-light driven nitrogen-modified commercial TiO₂ photocatalysts. *J. Hazard. Mater.* 2011, 190, 938–944.
- [16] Tian, H.; Ma, J.F.; Li, K.; Li, J.J. Hydrothermal synthesis of S-doped TiO₂ nanoparticles and their photocatalytic ability for degradation of Methyl orange. *Ceram. Int.* 2009, 35, 1289–1292.
- [17] Chen, C.C.; Lua, C.S.; Chung, Y.C.; Jan, J.L. UV light induced photodegradation of malachite green on TiO₂ nanoparticles. *J. Hazard. Mater.* 2007, 141, 520–528.
- [18] Ullmann's Encyclopedia of Industrial Chemistry. Part A27. Triarylmethane and Diarylmethane Dyes; 6th ed.; Wiley-VCH; New York, 2001.
- [19] R. Bonnett, G. Martinez, Photobleaching of sensitizers used in photodynamic therapy. *Tetrahedron* 57 (2001) 9513-9547.
- [20] Cho, B.P.; Yang, T.; Blankenship, L.R.; Moody, J.D.; Churchwell, M.; Bebland, F.A.; Culp, S.A. Synthesis and characterization of N-demethylated metabolites of malachite green and leucomalachite green. *Chem. Res. Toxicol.* 2003, 16, 285-294.
- [21] Sobana, N.; Krishnakumar, B.; Swaminathan, M. Synergism and effect of operational parameters on solar photocatalytic degradation of an azo dye (Direct Yellow 4) using activated carbon-loaded zinc oxide. *Mater. Sci. Semicond. Process.* 2013, 16, 1046–1051.
- [22] sun, J.H.; Wang, Y.K.; Sun, R.S.; Dong, S.V. Photodegradation of azo dye Conco Red from aqueous solution by the WO₃-TiO₂/ activated carbon (AC) photocatalyst under the UV irradiation. *Mater. Chem. Phys.* 2009, 155, 303-308.
- [23] Kumar, J.; Bansal, A. Dual effect of photocatalysis and adsorption in degradation of Azorubine dye using nanosized TiO₂ and activated carbon immobilized with different techniques. *Int. J. Chem. Tech. Res.* 2010, 1, 1537-1543.
- [24] Chen, C.; Yu, B.; Liu, J.; Dai, Q.; Zhu, Y. Investigation of ZnO films on Si(111) substrate grown by low energy O⁺ assisted pulse laser deposited technology. *Mater. Lett.* 2007, 61, 2961-2964.
- [25] Rahmatollah Rahimi, Samaneh Safalou Moghaddam, Mahboubeh Rabbani, Comparison of photocatalysis degradation of 4-nitrophenol using N,S co-doped TiO₂ nanoparticles synthesized by two different routes, *J Sol-Gel Sci Technol* (2012) 64:17–26

- [26] Subash, B.; Krishnakumar, B.; Swaminathan, M.; Shanthi, M. Highly efficient, solar active and reusable photocatalyst: Zr-loaded Ag–ZnO for Reactive Red 120 dye degradation with synergistic effect and dye-sensitized mechanism. *Langmuir*. 2013, 29, 939–949.
- [27] Subramanian Balachandran, Natarajan Prakash, Kuppulingam Thirumalai, Manickavachagam Muruganandham, Mika Sillanpa and Meenakshisundaram Swaminathan, pubs.acs.org/doi/10.1021/ie404287m | *Ind. Eng. Chem. Res.*
- [28] K. Ameta, P. Tak, D. Soni and suresh, C.ameta. *Sci. Revs. Chem. Commun.*, 2014, 4, 38-45.
- [29] B. Subash, B. Krishnakumar, M. Swaminathan, and M. Shanthi, *Langmuir.*, 2013, 29, 939–949.
- [30] Gusfiyesi, Admin Alif, Hermansyah Aziz, Syukri Arief and Edison Munaf. *Res. J. Pharm. Biol. Chem. Sci.*, 2014, 5, 918.
- [31] Q. Xiang, Jiaguo Yu and Mietek Jaroniec, *Phys. Chem. Chem. Phys.*, 2011, 13, 4853–4861 4853.
- [32] K.I. Ishibashi, A. Fujishima, T. Watanabe and K. Hashimoto, *Electrochem. Commun.*, 2000. 2, 207–10.

(Received 17 February 2015; accepted 23 February 2015)