Poll Res. 39 (4) : 1175-1179 (2020)
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ISSN 0257–8050

COMPARATIVE PHOTOCATALYTIC DEGRADATION OF THIAZINE DYES OVER VISIBLE LIGHT ACTIVE NICKEL BISMUTH IODIDE

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(Received 28 February, 2020; Accepted 19 May, 2020)

ABSTRACT

In this work, Nickle Bismuth Iodide nanoparticles were successfully synthesized by simple precipitation and solid-state methods. The as-synthesized photocatalyst was characterized through XRD, FESEM, EDX UV-Vis analysis. To investigate the photocatalytic activity of Nickle Bismuth Iodide, photooxidation of Azure-A and Toluidine blue was comparatively studied. The impact of several factors like pH, the concentration of Azure-A and Toluidine blue dyes, amount of Nickel Bismuth Iodide, and irradiation time were examined. Increment in the reaction rate of both dyes was monitored with the help of a spectrophotometer. A tentative mechanism has been proposed for photocatalytic decomposition of both the dyes. The experimental results show that both dyes degrade approx 85% under the visible light.

KEY WORDS : XRD, FESEM, EDS, DRS, Nickel Bismuth Iodide.

INTRODUCTION

The discharge of several contaminants such as phenols, dyes, hydrocarbons, sulfur, nitrogen, other organic compounds, and heavy metal are the main cause of water pollution (Ahmed *et al.,* 2013). Among them, dyes release from textile industries is a major threat to the environment. To eliminate dyes from wastewater 'Semiconductor photocatalysis' is a green and promising method compared to other reported processes (Lin *et al.,* 2012). In recent years, titanium dioxide and its various modified forms are considered the most suitable photocatalyst that involves degradation and removal of various toxic dyes (Saha *et al.,* 2012, Zhao *et al.,* 2010 and Safajou *et al.,* 2017). TiO_2 can not be able to produce an electron-hole pair by using the wavelength of the visible light region due to its wide bandgap. Hence, Visible-light-induced photocatalyst is invented by the researchers (Ma *et al.,* 2010).

Visible light activity in TiO_2 could be introduced by dopping (Asahi *et al.,* 2001). Seery *et al.* (2007) reported silver dopped TiO_2 nanomaterial to increase the visible light absorption efficiency of TiO_2. The degradation of acetaldehyde and isopropyl alcohol can be degraded with the help of visible light reported by Kim *et al.* (2005).

Researchers reported the degradation of many toxic organic contaminants by Iodide compounds and its various modifications. Feng *et al.* (2017) studied the 100% degradation of phenol, bisphenol-A, and hydroquinone using a combination of peroxymonosulphate (PMS) and iodide ions (I^-). Rapid selective circumneutral degradation of phenolic pollutants using PMS iodide metal-free oxidation. Sun *et al.* (2018) synthesized gold/copper iodide (Au/CuI) which shows a new application of ethanol oxidation and organic contaminants degradation by using plasmonic photoelectron catalysts under visible light irradiation. Ren *et al.* (2018) investigated the degradation of sulfamethoxazole with the help of Z-scheme AgI/Ag/Bi_3TaO_7 new type of visible light-responsive photocatalyst. It shows high efficiency to degrade oxcarbazepine, rhodamine-B, and X-3B. Hamdi *et al.* (2020) carried out the degradation of phenol and photocatalytic activity of antimony, iodide and rare earth metal on SnO_2.

The present work aims to synthesize a Nickel Bismuth Iodide photocatalyst. The photocatlytic

activity of Nickel Bismuth Iodide was investigated for a class of thiazine dyes. The comparative study of Azure-A and Toluidine blue was chosen as model pollutants in wastewater.

MATERIALS AND METHODS

Materials

All the chemicals used in the synthesis process and photocatalytic process were analytical grade. $Ni(NO_3)_2.6H_2O$, KI and $Bi(NO_3)_3.5H_2O$ are purchased from Merck company and used as without further purification.

Synthesis of Nickel Bismuth Iodide

The nanoparticles Nickel Bismuth Iodide was synthesized by using 0.1M concentration of precursors. In first step initial iodides NiI_2 and BiI_3 were synthesized by co-precipitation method from Nickel nitrate and Bismuth nitrate which further followed solid-state reaction to synthesized Nickel Bismuth Iodide.[12]

In the first step, NiI_2 (Black) precipitation was synthesized by using 0.1M concentration of $Ni(NO_3)_2.6H_2O$. It was dissolved in a minimum amount of distilled water to prepare its aqueous solution. After that approx 8 mL of concentrated HNO_3 was added which showed a common ion effect and after stirring for 5 min with a magnetic stirrer at room temperature, while stirring 0.1M aqueous solution, KI was added dropwise into the Nickel nitrate solution to obtain a black precipitate of NiI_2. Similarly, BiI_3 was synthesized by using 0.1M $Bi(NO_3)_3.5H_2O$, concentrate HNO_3 and 0.1M KI.

Finally, Nickel Bismuth Iodide was synthesized by mixing NiI_2 and BiI_3 in a 1:1 mole ratio and ground in mortar. The resulting powder was heated at a relatively low temperature of about 50-60 ^oC in the oven for 8h. After proper heating, it was allowed to cool naturally at room temperature.

Characterization

Field emission scanning electron microscopy (FESEM/EDX) images were obtained on Hitachi-PU 5.0kV to obtained its morphology and elemental analysis. DRS spectra were recorded using a UV-Vis spectrophotometer Hitachi 330 (Perkin Elmer UV Win Lab 6.0.3.0730/1.61.00 Lambda 900).

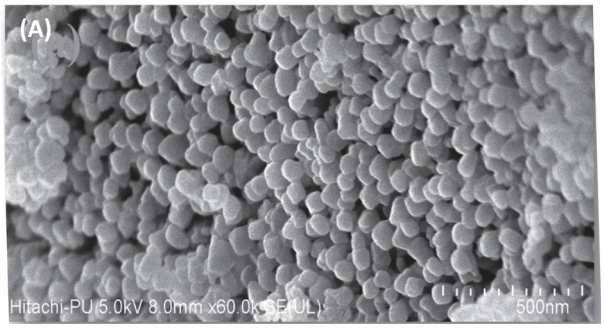
Photocatalytic test

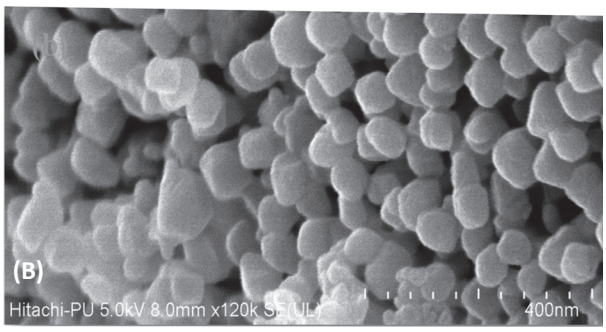
The efficiency of Nickel Bismuth Iodide was investigated by degrading Azure-A and Toluidine blue dye under visible light irradiation. The photodegradation reaction rate was monitored by measuring the optical density. The solution of Azure-A dye having catalyst is exposure under visible light for 100 min and sampling was done at 10 min intervals. The change in absorbance versus time was observed using a visible spectrophotometer (Chino) at the absorption band maximum 600 nm and 590 nm. Irradiation was carried out by exposure of 200 W tungsten lamp (Philips, light intensity = 70 mW/cm^2) as a source of visible light. The light intensity was determined from the solarimeter (Surya Mapi Model CEL 201) in a unit of mW/cm^2. A cut off water filter was placed on the reaction mixture to remove any thermal radiation.

RESULTS AND DISCUSSION

FESEM and EDX analysis

Fig.1(a-c) shows field emission electron micrograph of Nickel Bismuth Iodide synthesized at low temperature. When the mole ratio was selected to 1:1 the shape of both iodides BiI_3 and NiI_2 are distributed in pebbles shapes or spherical shapes uniformly. Chemical purity of as prepared Nickel Bismuth Iodide photocatalyst has been investigated by Electron Diffraction X-ray spectroscopy (EDS). Fig. 2 shows the product contains Ni, Bi, and I. The





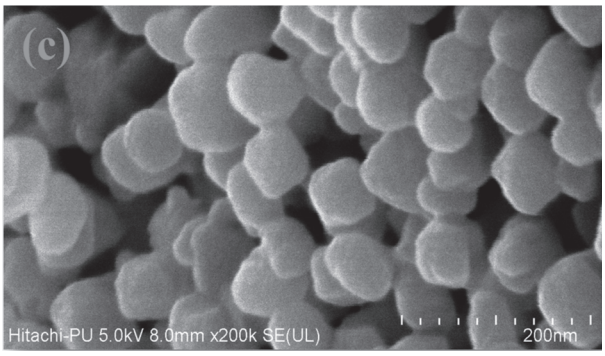


Fig. 1. (a-c) FESEM images for Nickel Bismuth Iodide at various magnification.

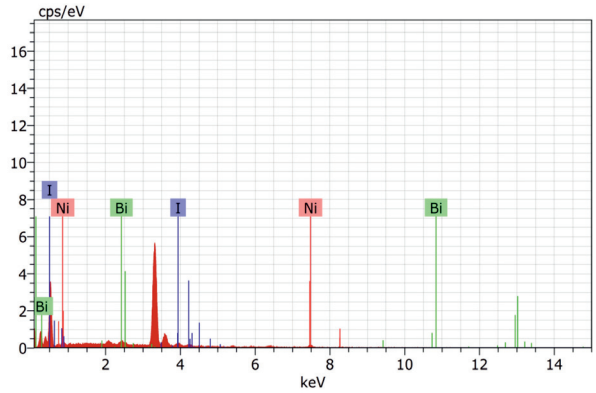


Fig. 2. EDX Image of Nickel Bismuth Iodide.

EDS spectrum shows no other peaks for any other element which conforming to the purity of the phase in the catalyst.

UV-Vis NIR spectroscopy analysis

The optical band gap (Eg) may be evaluated based on the optical absorptions spectrum using the following equation-

$$(ah\upsilon)^2 = B(h\upsilon) - Eg)$$

Where hυ is the photon energy, A is absorbance, B is a material constant and n is 2 or ½ for direct and indirect transitions, respectively. So the bandgap of the product was obtained from the extrapolation of $(ah\upsilon)^2$ versus hυ curve represented in Fig. 3. The optical band gap of Nickel Bismuth Iodide was calculated to 2.25 eV.

Photocatalytic Degradation

The optical density of the experimental solution was studied by spectrophotometrically at λ_{max} 600 nm for Azure-A and 590 nm for Toluidine blue. The required pH of the reaction mixture was obtained by adding standard 0.1 N HCl and 0.1N sodium hydroxide solution. The experimental solution was

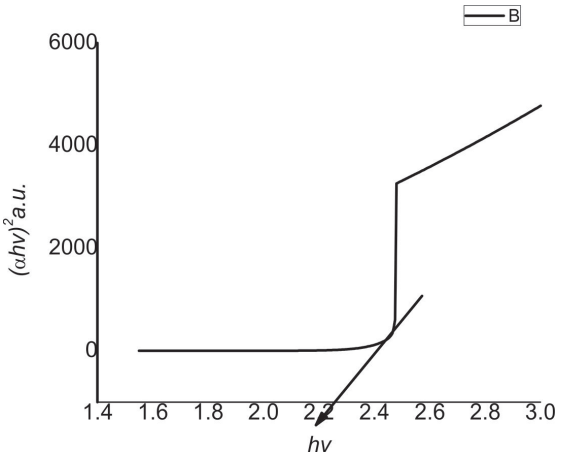


Fig. 3. Plot of $(a\lambda\upsilon)^2$ versus photon energy (λυ).

illuminated with a 200 W tungsten lamp. The 100 ml. beaker was filled with 50 mL of the reaction mixture and approx 3 mL of the sample were drawn. After every 10 min, the sample was examined under spectrophotometer. The optical density for both solutions decreased with increasing time. A linear line was obtained from the graph between 1+log A and time. The rate constant can be calculated using the following equation k = 2.303 x slope. Rate of reaction for Azure-A = 2.30 x 10^{-4} and for Toluidine blue = 2.61 x 10^{-4} was obtained according to degradation graph represented in Fig. 4 and 5.

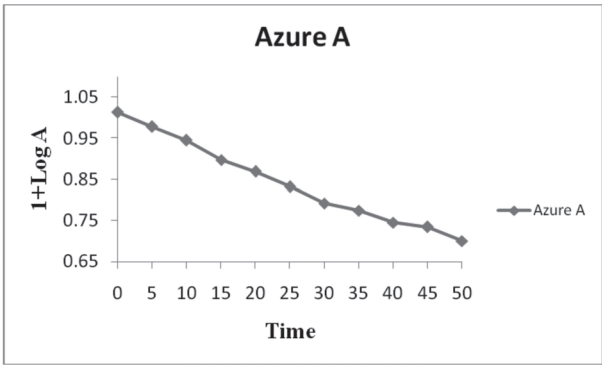


Fig. 4. A Typical Run for Azure-A

EFFECT OF DIFFERENT PARAMETERS

Effect of pH

Effect of pH on degradation of Azure-A and Toluidine blue was examined from 2 to 10 pH. the results are graphically represented in Fig. 6 it was concluded from experimental results that after a particular value that is 6 pH on increasing the pH rate of reaction will be decreased. At 6 pH both dyes

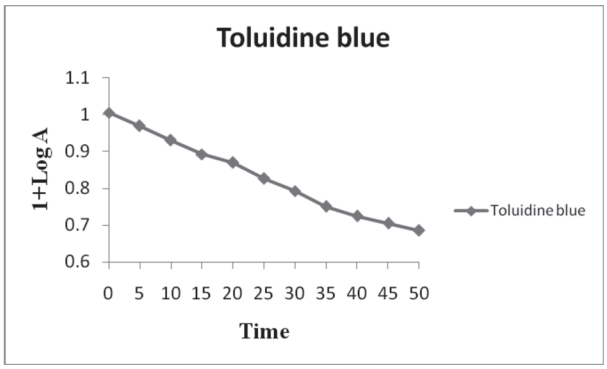


Fig. 5. A typical run for Toluidine blue

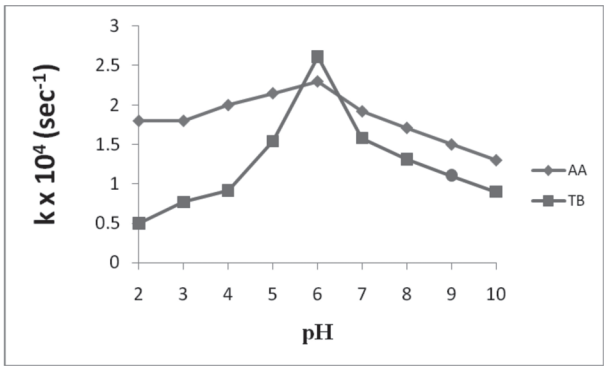


Fig. 6. Effect of pH.

show maximum degradation which is a great advantage due to its high efficiency in neutral medium. (Saroyan *et al.,* 2019)

Effect of Concentration

The molality was varied from 5.5 x 10^{-5} to 8.5 x 10^{-5} M for AA and 3.5 x 10^{-5} to 6.5 x 10^{-5} M for TB. The results are graphically shown in Fig. 7. The

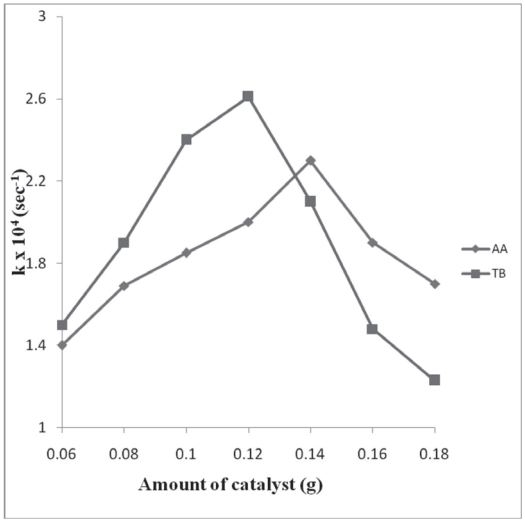


Fig. 7. Effect of Catalyst Dose

experimental results indicate that after the optimum value further increasing the concentration will decrease the rate of reaction. It is due to after the maximum value dye molecules act as inter filter and will not permit incident light to reach the surface of Nickel Bismuth Iodide (Babu *et al.,* 2019).

Effect of Catalyst Dose

The amount of catalyst was varied from 0.06 g to 0.18 g. The experimental results represent in fig.8 from the results it was observed that after the corresponding value (0.14 g for AA and 0.12 g for TB) in increasing the amount of catalyst will only increase the aggregation of catalyst particles. Hence, after the maximum degradation value, the increment in the amount of catalyst will retard the rate of reaction. (Jayaraman *et al.,* 2020).

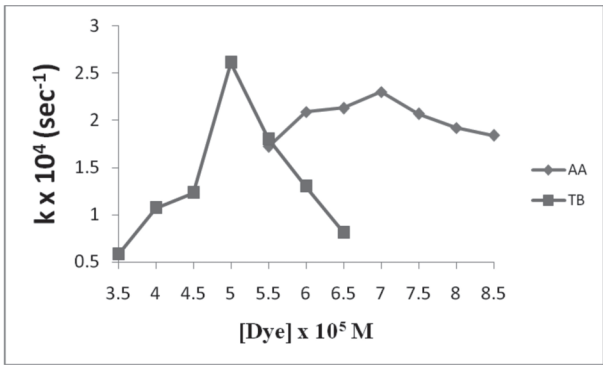


Fig. 8. Effect of Dye Concentration

Effect of Light Intensity

The light intensity was varied from 30 to 70 mW/ Cm^2. The rate of reaction will increase by increasing the intensity of light. It is due to more photons are available to strike on the surface of Nickel Bismuth Iodide and it will promote an electron from the lower state to the excited state. After the optimum value, negligible changes noticeable in the rate of degradation. The results are represented graphically

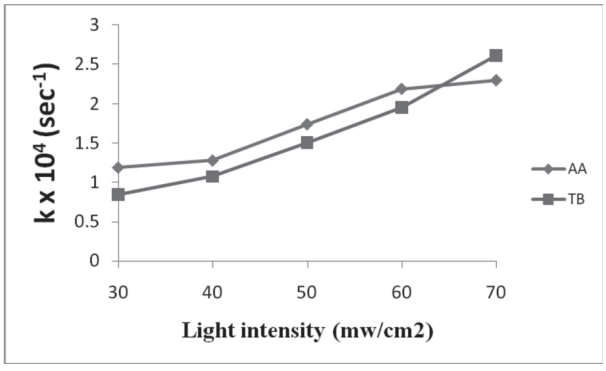


Fig. 9. Effect of Light Intensity

in Fig. 9 (Samy *et al.,* 2020).

Mechanism

A light of suitable wavelength was absorbed by the dye molecules due to this dyes undergoes its first singlet excited state. By the intersystem crossing, it will go to its triplet state. Same as Nickel Bismuth Iodide also absorbs suitable incident light and excited its electron in the conduction band from the valence band leaving a hole in the valence band and electron in the conduction band. This hole is responsible for generating hydroxyl radical due to absorbing by hydroxyl ion. This hydroxyl radical convert dye molecules to its leuco form which subsequently convert into the less harmful molecules. A tentative mechanism is as follows-

(1) $^1Dye_0$ (AA and TB) $\rightarrow$ $^1Dye_1$ (AA and TB)

(2) $^1Dye_1$ (AA and TB) $\rightarrow$ $^3Dye_1$ (AA and TB)

(3) $NiBiI_5 \rightarrow NiBiI_5$ [e^- (CB) + h^+ (VB)]

$h^+ + {}^-OH \rightarrow {}^\bullet OH$

$H_2O + h^+ \rightarrow H^+ + {}^\bullet OH$

Dye (AA and TB) + $^\bullet$OH $\rightarrow$ Leuco (AA and TB)

Leuco Dye (AA and TB) $\rightarrow$ Products

CONCLUSION

Nickel Bismuth Iodide photocatalyst has been made up of reaction of NiI_2 and BiI_3 in solid-state reaction. The optical property of Nickel Bismuth Iodide was studied by Diffuse reflectance spectra and it was observed that the product can active in the visible range. It shows significance degradation for Toluidine blue as well as for Azure – A. Favorable condition for Toluidine blue were pH= 6, [TB] = 5.0×10^{-5} M, Nickel Bismuth Iodide amount = 0.12 g, light intensity = 70mw/cm^2. For Azure –A pH= 6, [AA] = 7.0×10^{-5} M, Nickel Bismuth Iodide amount = 0.14 g, light intensity = 70mw/cm^2.

REFERENCES

Ahmed, M.A., Gharni, Z.H. and Katori, E.E. 2013. Photocatalytic degradation of methylene blue using Fe_2O_3/TiO_2 nanoparticles prepared by the sol-gel method. *J. Alloys. Compd.* 553 : 19-23.

Asahi, R. Aoki, K. Morikawa, T. Ohwaki, T. and Taga, Y. 2001. Visible-light photocatalysis N-dopped TiO_2. *Science.* 293 : 269-271.

Babu, S.G. Jhon M.C. Kartik, P. Khim, J. Kumar, M.A. Lakhera, S.K. and Neppolian, B. 2019. Synergetic effect of a sono-photocatalytic process for the degradation of organic pollutants using CuO-TiO_2/rGO. *Ultrason. Sonochem.* 50 : 218-223.

Feng, Y. Lee, P.H. Shih, K. and Wu, D. 2017. Rapid selective circum neutral degradation of phenolic pollutants using peroxymonosulfate-iodide metal free oxidation: Role of iodine atoms. *Environ. Sci. Technol.* 51 : 2312-2320.

Hamdi, A.M. 2020. Synthesis and comparison of the photocatalytic activities of antimony, iodide and rare earth metals or SnO_2 for the photodegradation of phenol and it's intermediate under UV, solar and visible light irradiation. (Book)

Jayarama, S. and Warrier, A.R. 2020. Dark catalytic degradation of industrial dye effluents using orthorhombic Tin monosulfide nanocatalyst. *J. Mol. Liq.* 307: 112360.

Kim, H.G. Borse, P.H. Choi, W. and Lee, J.S. 2005. Photocatalytic nanodiodes for visible light photocatalysis. *J. German Chem. Soci.* 44: 4585-4589.

Lin, H., Cao, J. Luo, B. and Xu, B. 2012. Synthesis of novel Z-scheme AgI/Ag/AgBr composite with enhanced visible light photocatalytic activity. *Catalysis*. 21 : 91-95.

Ma, X. Y., Chen, Z. G. Hartono, S. B. Jiang, H. B. Zou, J. Qiao, S. Z. and Yang, H. G. 2010. Fabrication of uniform anatase TiO_2 particles exposed by {001} facets. *Chem. Commun.* 46 : 6608-6610.

Ren, M., Ao, Y., Chen, J., Hou, J., Quan, J. and Wang. C. 2018. Construction of silver iodide/ silver/bismuth tantalite Z-scheme photocatalyst for effective visible light irradiation of organic pollutants. *J. Colloid Interf. Sci.* 532 : 190-200.

Safajou, H. Derazkola, S.M. Khojasten, H. and Nisari, M.S. 2017. Enhanced photocatalytic degradation of dyes over graphene/Pd/TiO_2 nanocomposites: TiO_2 nanowires versus TiO_2 nanoparticles. *J. colloid Interf. Sci.* 498 : 423432.

Saha, S. Pal, A. and Wang, J.M. 2012. Nanosilver impregnation on commercial TiO_2 and a comparative photocatalytic account to degrade malachite green. *Sep. Purif. Technol.* 81 : 147-159.

Samy, M. Alalm, M.G. Fujii, M. and Ibrahim, M.G. 2020. Effective photocatalytic degradation of sulfamethazine by CNTs/$LaVO_4$ in suspension and dip coating modes. *Sep.Purif Technol.* 235: 116138.

Saroyan, H. Deliyanw, E.A., and. Kyzas, G.S. 2019. Effective dye degradation by graphene oxide supported manganese oxide. *Processes.* 7 : 40.

Seery, M.K. Floris, P. George, and R. Pillar, S.C. 2007. Silver doped TiO_2 nanomaterial for enhanced visible-light photocatalysis. *J. Photochem. Photobiol. A Chem.* 189 : 258-263.

Sun, M. Hu, J. Zhai, C. and Zhu, M. 2018. Plasmon enhanced electrocatalytic oxidation of ethanol and organic contaminants on gold/copper iodide composites under visible light irradiation. *J. Colloid Interf. Sci.* 511 : 110-118.

Zhao, W. Bai, Z. Guo, B. Ren, A. and Wu, C. 2010. Sunlight photocatalytic activity of CdS modified TiO_2 loaded on activated carbon fibers. *Appl. Surf. Sci.* 256: 3493-3498.