ENHANCEMENT OF PHOTOCATALYTIC ACTIVITY OF TIN OXIDE BY DOPING WITH NITROGEN

KAVITA RANAWAT, DIPTI SONI and SANYOGITA SHARMA[*]

Department of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA

ABSTRACT

In the present work, stannic oxide has been used as a photocatalyst to degrade basic fuchsin. The nanophotocatalysts pure SnO_2 and N-doped SnO_2 were prepared by precipitation method. The effect of variation of different parameters like pH, concentration of basic fuchsin, amount of photocatalyst, dopant percentage and light intensity on the rate of photocatalytic degradation was also observed.

Key words: SnO_2, N-doped SnO_2, Photocatalysis, Basic fuchsin.

INTRODUCTION

Water pollution by different hazardous compounds is becoming an increasing global concern.[1-3] The major industries that are participating in this process include leather, marble stone, distilleries, sugar, textile, pesticides, pharmaceuticals, pulp & paper mills, tanneries, dyes and dye intermediates, petro-chemicals, steel plants, etc. The improper treatment and inappropriate disposal of toxic carcinogenic compounds pose a considerable threat to the environment.[4]

A dye is a colored substance that has an affinity to the substrate, to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. The problem of bioaccumulation of dyes in the aquatic organisms is mounting because of the multiplying sources of the dye contamination, such as textile industry, food technology, paper and printing, cosmetic, pharmaceutical, detergent, pesticide and leather tanning industry, which in total consume more than one million tons of dyes annually.[5] Synthetic dyes are found in a wide range of products such as clothes, leather accessories, and furniture. Up to 12% of these dyes are wasted during the dyeing process and about 20% of this wastage enters the environment (mainly into water supply).[6] This results in colored, toxic and contaminated water bodies leading to reduction in sunlight penetration deep into the water and finally diminishing photosynthesis and as a result, flora and fauna are destroyed.

Considerable work has been carried out on the removal of dye from wastewater by adsorption, coagulation, flocculation, oxidation, precipitation, filtration, electrochemical processes, etc. and these are the common techniques reported for the removal of dyes from effluents[7]. But all these processes have many drawbacks involving high operating costs, and incapability to degrade dyes completely. Now-a-days,

_____

photocatalysis is supposed to be one of the best methods for removing the dyes from wastewater because of the ability of this method to completely mineralize the target pollutants. Photoelectrocatalytic process using semiconductor electrodes has been widely studied due to their inherent high catalytic activity for oxidation of organic pollutants in the past two decades[8,9].

Currently, many semiconductors have been applied in heterogeneous photocatalysis such as CdS, SnO_2, WO_3, TiO_2, $ZrTiO_4$, and ZnO. Many researchers reported that TiO_2, ZnO, and SnO_2 are the most active catalysts in the degradation of dyes, phenols, and pesticide.[10,11] Furthermore, these semiconductors have been recognized as preferable materials for photocatalytic processes due to their high photosensitivity, nontoxic nature, low cost, and chemical stability.[12-16] In the photocatalytic oxidation process, organic pollutant is decomposed in the presence of a wide-band gap semiconductor that can promote reactions in the presence of UV light without being consumed in the overall reaction.

Heterogeneous advanced oxidation processes (AOPs), involving photocatalyzed degradation of dyes using semiconductor nanoparticles is considered as an efficient cure for dye pollution. The availability of active sites on the material surface also plays a major role in the ability of the photocatalytic material to degrade organic contaminants[17]. SnO_2 has been used in a wide range of applications in science, technology and industries such as catalysts, semiconductor material, gas sensing, ceramics, plastics and biomedical applications.[18]

The photolysis of auramine O dye was performed using sunlight and SnO_2 as the photocatalyst. Yang et al.[19] synthesized $SnO_2/ZnO/TiO_2$ composite photocatalyst. They also tested its photocatalytic activity with photodecomposition of methyl orange under both; visible and UV light irradiations. Kuzhalosai et al.[20] reported that SnO_2 loaded ZnO (SnO_2–ZnO) was more efficient for the degradation of acid orange 10 than commercial ZnO, bare ZnO, TiO_2-P25 and TiO_2. The photocatalytic behavior of the SnO_2/V_2O_5 nanowires for the photodegradation of toluidine blue O dye under UV exposure was examined by Shahid et al.[21] Erkan et al.[22] reported the photocatalytic antimicrobial activity over TiO_2, SnO_2 and their Pd doped thin film samples against *Escherichia coli*, *Staphylococcus aereus*, *Saccharomyces cerevisiae* and *Aspergilus niger* spores. SnO_2 was found to show lower photocatalytic efficiency against *E. coli* with a 56% decrease in survival after 2 h illumination and a 68% decrease in survival of *E. coli* after palladium addition.

EXPERIMENTAL

500 mL solution of tin (II) chloride (0.08 M) and 500 mL solution of oxalic acid dihydrate (0.16 M) were prepared separately. Oxalic acid dihydrate solution was added slowly into aqueous solution of tin (II) chloride with continuous stirring using a magnetic stirrer at room temperature till a clear and homogeneous solution was obtained. Solution was continuously stirred for 30 min till white precipitates were observed. 1.0 N NaOH (as a precipitation agent) was added drop wise into the stirred solution maintaining pH at 8.0. Then solution was again stirred for 30 min and kept overnight. The white precipitate of SnC_2O_4 was obtained. The transparent supernatant of SnC_2O_4 solution was decanted. 50 g urea was added as a carbon precursor to this wet precipitate and stirred using a magnetic stirrer for 1 hour. The precipitate was filtered and washed 6-7 times using distilled water for complete removal of chloride ions. Then precipitate was dried in oven at 70˚C-80˚C till it gets completely dried. Finally, dried compound was calcined in a muffle furnace at 800˚C for 1 hour to obtain nitrogen doped SnO_2.

All the solutions were prepared in doubly distilled water. The photocatalytic degradation of the dye was observed by taking dye solution and stannic oxide together. Irradiation was carried out by keeping the whole assembly exposed to a 200 W tungsten lamp (light intensity = 60.0 mW·cm^{-2}). The intensity of light at various distances from the lamp was measured with the help of a solarimeter. The pH of the solution was measured with the help of digital pH-meter. 0.0366 g of basic fuchsin was dissolved in 100 mL of doubly

distilled water to prepare their 1.0×10^{-3} M solution, which was used as stock solution. The stock solution was further diluted as and when required. The absorbance of the dye solution were determined with the help of a spectrophotometer at λmax = 550 nm. The progress of reaction was observed by measuring absorbance of the reaction mixture at regular time interval during exposure. Decreasing trend of absorbance showed that dye was degraded during this process. A decrease in absorbance of basic fuchsin solution was observed with increasing time of exposure. A plot of 1 + log A against time was found linear for pure SnO_2 and nitrogen doped SnO_2, which indicates that the degradation of basic fuchsin followed pseudo-first order kinetics. The rate constant was measured with the help of equation.

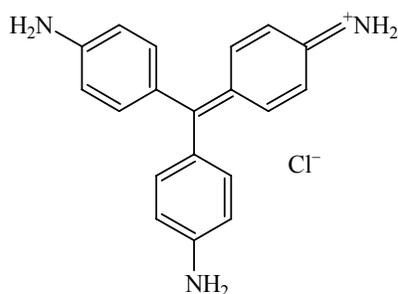$$k = 2.303 \times slope \qquad \qquad \ldots(1)$$

Fig. 1: Structure of basic fuchsin

RESULTS AND DISCUSSION

Various factors, which affect degradation of basic fuchsin dye have been studied to get the conditions for optimum degradation rate.

Effect of pH

The effect of pH on the rate of degradation of N-doped SnO_2 was investigated in the pH range 5.0 to 10.0. The results are graphically represented in Fig. 2.
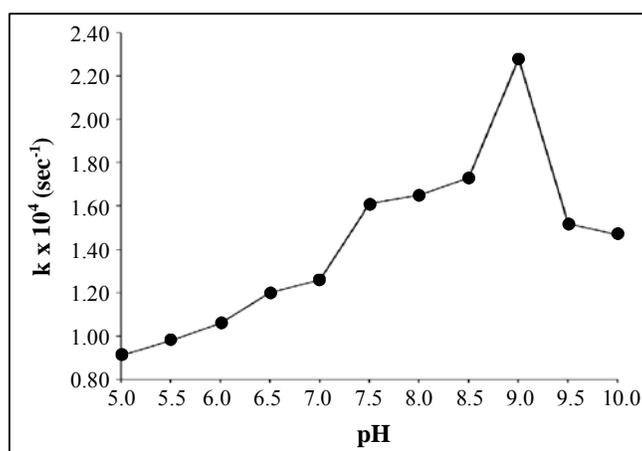

Fig. 2: Effect of pH

It has been observed that the rate of photocatalytic degradation of basic fuchsin increases as pH was increased and it attained optimum value at pH 9.0. The rate was decreased, when pH of the dye solution was further increased. It may be due to the fact that on increasing the pH of the solution, there is an attraction

between cationic dye molecule and negatively charged ⁻OH ions. But, at higher pH, the cationic dye molecules are converted into neutral form and hence, there is no attraction between neutral dye molecule and negatively charged surface of semiconductor. As a result, the rate was retarded.

Effect of basic fuchsin concentration

Effect of variation of dye concentration on the rate of reaction was also studied by taking different concentrations of basic fucshin solution. The results are presented graphically in Fig. 3.
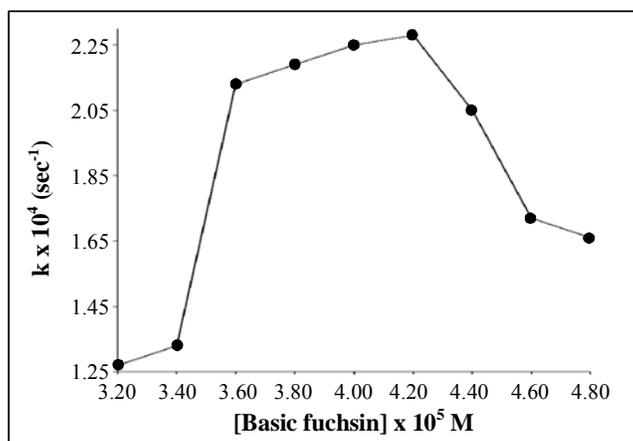

Fig. 3: Effect of basic fuchsin concentration

It was observed that the rate of photocatalytic degradation of dye increases on increasing the concentration of basic fucshin upto 4.20×10^{-5} M. It may be attributed to the fact that as the concentration of basic fucshin was increased, more dye molecules were available for excitation and consecutive energy/ electron transfer and hence, an increase in the rate of degradation of the dye was observed. There was a decrease in degradation rate on increasing the concentration of dye above 4.20×10^{-5} M. This may be due to the fact that after a particular concentration, the dye may start acting as an internal filter and it will not permit the sufficient light intensity to reach the surface of the photocatalyst at the bottom of reaction vessel.

Effect of amount of N-doped SnO₂

The effect of amount of N-doped stannic oxide on the rate of photodegradation of basic fuchsin was observed by keeping all other factors identical. The results are graphically represented in Fig. 4.
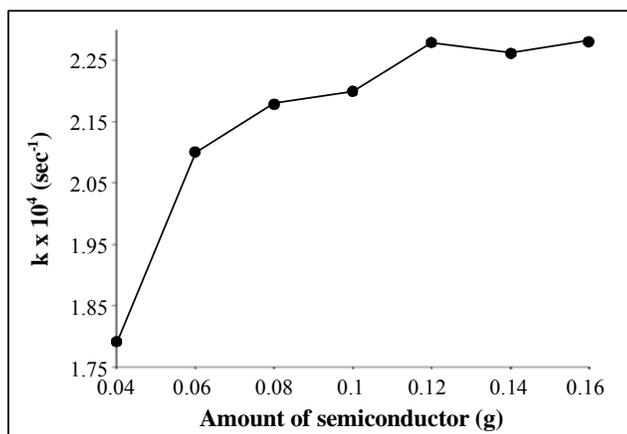

Fig. 4: Effect of amount of N-doped SnO₂

The rate of reaction was found to increase on increasing the amount of semiconductor, N-doped stannic oxide. The rate of degradation reached to its optimum value at 0.12 g of the photocatalyst, because as the amount of the semiconductor was increased, it provides more exposed surface area for degradation of dye molecules. Beyond 0.12 g, the rate of reaction becomes almost constant. After a particular value (0.12 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

Effect of light intensity

The effect of light intensity on the photodegradation of basic fuchsin was also observed. The results are graphically presented in Fig. 5.
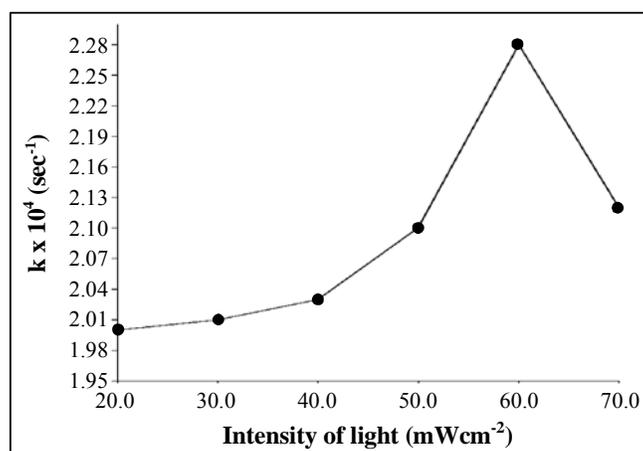

Fig. 5: Effect of light intensity

These data indicate that photocatalytic degradation of basic fuchsin was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photocatalyst surface. There was a decrease in the rate of reaction as the intensity of light was increased beyond 60.0 m Wcm^{-2}.

A typical run

After keeping the values of all the parameters constant for maximum rate constant, a typical run was observed for the photocatalytical degradation of the dye. The results are shown in Table 1 and graphically presented in Fig. 6. Here, a comparative observation was made for pure SnO_2 and N-doped SnO_2, which confirms that the rate was higher in the case of N-doped SnO_2 as compared to pure SnO_2.

Table 5: A typical run

[Basic fuchsin] $= 4.20 \times 10^{-5}$ M			N-doped SnO_2 = 0.12 g	
Light intensity = 60.0 mWcm^{-2}			pH = 9.0	
Time (min.)	**Pure SnO_2 Absorbance (A)**	**1 + log A**	**N-doped SnO_2 Absorbance (A)**	**1 + log A**
0	0.709	0.8506	0.709	0.8506
10	0.610	0.7853	0.625	0.7958

Cont…

Time (min.)	Pure SnO_2 Absorbance (A)	$1 + \log A$	N-doped SnO_2 Absorbance (A)	$1 + \log A$
20	0.590	0.7708	0.521	0.7168
30	0.507	0.7050	0.461	0.6637
40	0.448	0.6512	0.401	0.6031
50	0.389	0.5910	0.359	0.5550
60	0.371	0.5705	0.296	0.4712
70	0.325	0.5118	0.282	0.4502

Rate constant (k): For pure $SnO_2 = 1.90 \times 10^{-4} \ sec^{-1}$

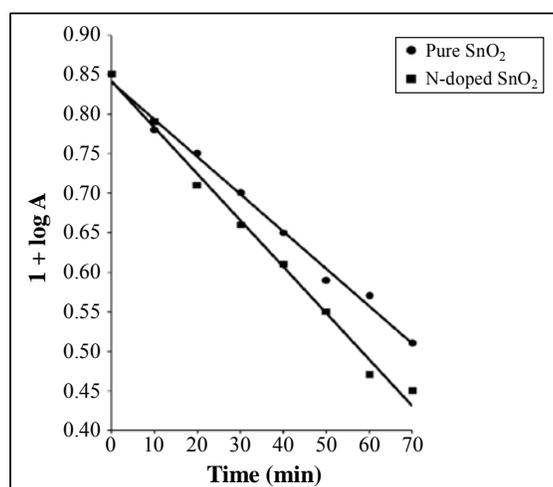For N-doped $SnO_2 = 2.28 \times 10^{-4} \ sec^{-1}$

Fig. 6: A typical run

Mechanism

On the basis of the experimental observations, a tentative mechanism of photocatalytic degradation of basic Fuchsin may be proposed as-

Basic fuchsin (BF) absorbs radiation of suitable wavelengths and it is excited to its first singlet excited state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting nitrogen doped stannic dioxide also utilize the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to products.

$$^1BF_0 \xrightarrow{\ h\nu\ } {}^1BF_1 \qquad \qquad \text{…(3.1)}$$

$$^1BF_1 \xrightarrow{\ ISC\ } {}^3BF_1 \qquad \qquad \text{…(3.2)}$$

$$SC \xrightarrow{\ h\nu\ } e^- \ (CB) + h^+ \ (VB) \qquad \qquad \text{…(3.3)}$$

$$h^+ + {}^-OH \longrightarrow {}^\bullet OH \qquad \qquad \text{…(3.4)}$$

$$^\bullet OH + {}^3BF_1 \longrightarrow Products \qquad \qquad \text{…(3.5)}$$

The participation of $^{\bullet}$OH radical as an active oxidizing species was confirmed by using hydroxyl radical scavenger (isopropanol), where the rate of degradation was drastically reduced.

The observations revealed that basic fuchsin dye could be degraded successfully by using N-doped SnO_2 under visible light. It was found that the N-doped SnO_2 has enhanced photocatalytic activity than pure SnO_2.

REFERENCES

1. A. K. Chakraborty, S. Ganguli and A. M. Kebede, Photocatalytic Degradation of 2-Propanol and Phenol Using Au Loaded $MnWO_4$ Nanorod under Visible Light Irradiation, J. Clust. Sci., **23**, 437-448 (2012).

2. X. Huang, M. Sillanpa, E. T. Gjessing and R. D. Vogt, Water Quality in the Tibetan Plateau: Major Ions and Trace Elements in the Headwaters of Four Major Asian Rivers, Sci. Total Environ., **407**, 6242-6254 (2009).

3. X. Huang, M. Sillanpa, B. Duo and E. T. Gjessing, Water Quality in the Tibetan Plateau: Metal Contents of Four Selected Rivers, Environ. Pollut., **156**, 270-277 (2008).

4. S. C. Ezeonu, R. Tagbo, N. E. Anike, A. O. Oje and E. N. I. Onwurah, Biotechnological Tools for Environmental Sustainability: Prospects and Challenges for Environments in Nigeria: A Standard Review, Biotechnol. Res. Int., 2012:450802 (2012). doi:10.1155/2012/450802.

5. Booth, Gerald, Dyes, General Survey, Wiley VCH (2000). doi:10.1002/14356007.a09_073.

6. M. A. Rauf and S. S. Ashraf, Fundamental Principles and Application of Heterogeneous Photocatalytic Degradation of Dyes in Solution, Chem. Engg. J., **151**, 10-18 (2009).

7. H. S. Peavy and D. R. Rowe, Environmental Engineering, McGraw-Hill (1985).

8. G. Waldner, M. Pourmodjib, R. Bauer and M. Neumannspallart, Photoelectrocatalytic Degradation of 4-Chlorophenol and Oxalic Acid on Titanium Dioxide Electrodes, Chemosphere, **50(8)**, 989-998 (2003).

9. C. Xiao-Fang, L. Wen-Hua, P. Ou-Yang, Z. Zhao, Z. Jian-Qing and C. Chu-Nan, Enhancement of Photocatalytic Activity of TiO_2 Film Electrode by *In Situ* Photoelectro-Generating Active Chlorine [J], Trans Nonferrous Met. Soc. China, **17(5)**, 1087-1092 (2007).

10. L. Zhang, J. Liu, C. Tang, J. Lv, H. Zhang, Y. Zhao and X. Wang, Palygorskite and SnO_2–TiO_2 for the Photodegradation of Phenol. Appl. Clay Sci., **1**, 68-73 (2011).

11. V. Kruefu, H. Ninsonti, N. Wetchakun, B. Inceesungvorn, P. Pookmanee and S. Phanichpant, Photocatalytic Degradation of Phenol Using Nb-Doped ZnO Nanoparticles, Eng. J. Can., **163**, 90-99 (2012).

12. B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan, Solar/UV-Induced Photocatalytic Degradation of Three Commercial Textile Dyes, J. Hazard. Mater., **89**, 303-317 (2002).

13. I. K. Konstantinou and T. A. Albanis, Photocatalytic Transformation of Pesticides in Aqueous Titanium Dioxide Suspension Using Artificial and Solar Light: Intermediates and Degradation Pathways, Appl. Catal. B, **42**, 319-335 (2003).

14. S. Senthilkumaar, K. Porkodi and R. Vidyalakshmi, Photodegradation of a Textile Dye Catalyzed by Sol-Gel Derived Nanocrystalline TiO_2 Via Ultrasonic Irradiation, J. Photochem. Photobiol., **170**, 225-232 (2005).

15. B. B. Lakshmi, C. P. Patrissi and C. R. Martin, Sol–Gel Template Synthesis of Semiconductor Oxide Micro and Nanostructures, Chem. Mater., **9**, 2544-2550 (1977).

16. K. Hara, T. Horiguchi, T. Khinoshita, K. Sayama, H. Sugihara and H. Arakawa, Highly Efficient Photon-to-Electron Conversion with Mercurochrome-Sensitized Nanoporous Oxide Semiconductor Solar Cells, Sol. Energy Mater. Solar Cells, **64**, 115-134 (2000).

17. O. Carp, C. L. Huisman and A. Reller, Photoinduced Reactivity of Titanium Dioxide, Prog. Solid State Chem., **32(1-2)**, 33-177 (2004).

18. J. A. T. Antonio, R. Gutierrez-Baez, P. J. Sebastian and A. Vazquez, Thermal Stability and Structural Deformation of Rutile SnO_2 Nanoparticles, J. Solid State Chem., **174**, 241-248 (2003).

19. G. Yang, Z. Yan and T. Xiao, Preparation and Characterization of $SnO_2/ZnO/TiO_2$ Composite Semiconductor with Enhanced Photocatalytic Activity, Appl. Surf. Sci., **258(22)**, 8704-8712 (2012).

20. V. Kuzhalosai, B. Subash, A. Senthilraja, P. Dhatshanamurthi and M. Shanthi, Synthesis, Characterization and Photocatalytic Properties of SnO_2–ZnO Composite under UV-A Light, Spectrochim. Acta, Part A, **115**, 876-882 (2013).

21. M. Shahid, I. Shakir, S. Yang and D. J. Kang, Facile Synthesis of Core-Shell SnO_2/V_2O_5 Nanowires and their Efficient Photocatalytic Property, Mater. Chem. Phys., **124(1)**, 619-622 (2010).

22. A. Erkan, U. Bakir and G. Karakas, Photocatalytic Microbial Inactivation Over Pd Doped SnO_2 and TiO_2 Thin Films, J. Photochem. Photobiol. A, **184(3)**, 313-321 (2006).