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ENHANCEMENT OF PHOTOCATALYTIC ACTIVITY OF TIN OXIDE BY NITROGEN DOPING

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ABSTRACT

In the present work, the nitrogen doped stannic oxide has been prepared by precipitation method and photocatalytic degradation of new fuchsin in presence of light has been carried out using this as prepared semiconductor. The photocatalytic degradation of the dye was monitored spectrophotometrically. The effect of various rate affecting parameters on the rate of reaction was observed. It was found that the nitrogen doped SnO_2 showed higher activity than the pure SnO_2 under visible light irradiation.

Key words: N-doped SnO_2, Photocatalyst, Photocatalytic degradation, New fuchsin.

INTRODUCTION

Environmental problems, especially, the sustained pollutions of water by various organic and metallic ion contaminants have been one of the most serious problems, and many efforts are dedicated to the remediation of environmental pollution.[1-3] As a result of the above, there arose an ever growing demand for eco-friendly methods to treat polluted water for its reuse. Researchers are constantly on the lookout for new and innovative methods that do not pollute our environment and at the same time these are effective enough to degrade the pollutants and clean and make the water reusable.

The industries based on dye stuff have become an essential need of developing society because these provide products of great variety. Dyes are able to color water even in concentrations as low as 1 mg/L. Textile wastewater contains typically a much higher amount of the dye content i.e. 10-200 mg/L, which gives intense coloration. While color is easily recognizable in the water stream, an additional environmental hazard comes from the fact that many dyes are either toxic or become toxic when being gradually decomposed in the ecosystem. Moreover, with the rapid development of the printing and dye industries; the effluents of these industries have become one of the most important water pollution sources. Effluents of the dye industries, which contain organic and inorganic impurities are discharged into water bodies without any further treatment. This problem of contaminated water can be effectively solved by photocatalytic process that removes impurities even in range of ppb and do not produce harmful side products.[4] Traditional

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wastewater treatments for printing and dyeing plants' effluents are mainly physical, chemical and biochemical methods.[5-7]

Heterogeneous photocataylsis is a widely accepted technique of choice for environmental purification. Dye degradation is a process in which the large dye molecules are broken down chemically into smaller molecules. The standard experimental set up for dye degradation photocatalysis is by using a UV lamp to provide energy for the creation of oxidizing radicals. Photocatalysis is the addition of light to a semiconductor oxide/sulphide that results in electrons moving from the valence band to the conduction band. The electron-hole pairs formed will react with oxygen and water molecules to create superoxide anions and hydroxide radicals that increase reducing and oxidizing abilities to be used on numerous industrial effluents.

Nanostructured semiconductors (such as TiO_2, ZnO, SnO_2 and so on) are proved to be excellent photocatalysts, which can degrade many kinds of persistent organic pollution.[8-14] Tin oxide (SnO_2), as one of the most important semiconductor oxides, has been used as photocatalyst for photodegradation of many organic compounds. The results showed that SnO_2 has exhibited good photoactivity toward degradation of dye and other organic compounds.[15,16] However, just like other transition metal oxides photocatalysts such as TiO_2 and ZnO, SnO_2 suffer from low photocatalytic efficiency because of its wide-bandgap (3.6 eV)[17] and high recombination rates of photogenerated electron-hole pairs. This defect hinders SnO_2 photocatalyst using widely and practically in the environmental application.[18]

Egzar et al.[19] carried out the photocatalytic degradation of aniline blue dye using different semiconductors such as ZnO, ZnS and SnO_2. It is noteworthy that ZnO/SnO_2 exhibited enhanced photodegradation ability for congo red, ascribed to the high adsorption capacity derived from the strong electrostatic interaction between ZnO/SnO_2 and congo red. Based on the investigation, it was found that these porous ZnO/SnO_2 hetero-nanofibers possess versatile potential applications for wastewater purification. Dai et al.[20] synthesized flower-like SnO_2 microstructures, which exhibited higher photoactivity (about 2.2 times) than granular SnO_2 for the degradation of rhodamine dye. It was observed that these structural features can improve both the sensing performance and the photocatalytic degradation rate.

Nanostructured semiconductor films of SnO_2, TiO_2 and SnO_2/TiO_2 have been employed for electrochemically assisted photocatalytic degradation of naphthol blue black. The degradation rate was found significantly higher for SnO_2/TiO_2 composite films than SnO_2 and TiO_2 films alone.[21,22] The photocatalytic activity of the coupled CeO_2–SnO_2 oxide ranged depending on the CeO_2 contents. The optimum amount of CeO_2 for the synthesis of CeO_2–SnO_2 was 7 wt.% since the nanoparticles showed high photocatalytic activity in the degradation of the dye, similar to that of the TiO_2–P25 photocatalyst. The kinetics of photocatalytic degradation and total organic carbon removal under sunlight were found to follow a first-order rate law. The results indicated that CeO_2–SnO_2 can be used for the removal of dyes from wastewater.[23]

EXPERIMENTAL

Preparation of N-doped SnO_2 nanoparticles

500 mL solution of tin (II) chloride (0.08 M) and 500 mL solution of oxalic acid dihydrate (0.16 M) were prepared separately. All the solutions were prepared in doubly distilled water. Oxalic acid 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. when white precipitates were observed. 1.0 N NaOH (as a precipitation agent) was added dropwise into the stirred solution until the pH was maintained 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 nitrogen precursor to this wet precipitate and using 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.

IUPAC name of new fuchsine is 4-[(4-aminophenyl)(4-iminocyclohexa-2,5-dien-1-ylidene)methyl]-2 methylaniline. Its molecular formula is $C_{22}H_{24}N_3Cl$. Its molecular weight is 365.9 $gmol^{-1}$. Its λ_{max} is 550 nm.

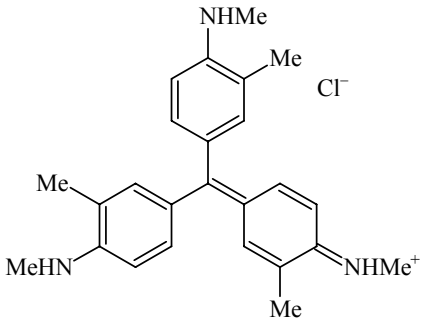

Fig. 1: Chemical structure of new fuchsin

New fuchsin dye has been used as a model system in the present investigation to compare the photocatalytic activity of pure SnO_2 and N-doped SnO_2. Irradiation was carried out by keeping the whole assembly exposed to a 200 W tungsten lamp (Philips; light intensity = 40.0 $mWcm^{-2}$). The intensity of light at various distances from the lamp was measured with the help of a solarimeter. The pH of the solutions was measured with the help of digital pH-meter. 0.0337 g of new 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 was determined with the help of a spectrophotometer at λ_{max} = 550 nm for new fuchsin. The progress of reaction was observed by measuring absorbance of the reaction mixture at regular time interval during exposure. A decrease in absorbance of new fuchsin solution was observed with increasing time of exposure. Decreasing trend of absorbance showed that dye was degraded during this process. A plot of 1 + log A against time was found linear for pure SnO_2 and nitrogen doped SnO_2, which indicated that the degradation of new fuchsin followed pseudo-first order kinetics. The rate constant was measured with the help of equation k = 2.303 × slope.

RESULTS AND DISCUSSION

Various factors, which affect degradation of new fuchsin dye have been studied to get the condition for optimum degradation rate and discussed below.

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 reported in Table 1.

It has been observed that the rate of photocatalytic degradation of new fuchsin increases as pH was increased and it attained optimum value at pH 9.5. 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 convert into neutral form and hence, there is less attraction between neutral dye molecule and negatively charged surface of semiconductor. As a result, the rate was retarded.

Table 1: Effect of pH

[New Fuchsin] = 3.80×10^{-5} M, N-doped SnO_2 = 0.10 g**,** Light intensity = 40.0 $mWcm^{-2}$

pH	**Rate Constant (k) × 10^4 (sec^{-1})**
5.0	1.43
5.5	1.46
6.0	1.54
6.5	1.85
7.0	2.13
7.5	2.19
8.0	2.27
8.5	2.41
9.0	3.08
9.5	**3.37**
10.0	1.76

Effect of new fuchsin concentration

Effect of variation of dye concentration on the rate of reaction was also studied by taking different concentration of new fuchsin solution. The results are tabulated in Table 2.

Table 2: Effect of new fucshin concentration

pH = 9.5, N-doped SnO_2 = 0.10 g**,** Light intensity = 40.0 $mWcm^{-2}$

[New fuchsin] × 10^5 M	**Rate constant (k) × 10^4 (sec^{-1})**
3.40	2.78
3.60	2.88
3.80	**3.37**
4.00	3.04
4.20	2.91
4.40	2.82
4.60	2.72

It was observed that the rate of photocatalytic degradation of dye was increased on increasing the concentration of new fuchsin upto 3.80×10^{-5} M. It may be attributed to the fact that as the concentration of the new fuchsin 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 3.80×10^{-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 SnO_2

The effect of amount of N-doped stannic oxide on the rate of photodegradation of new fuchsin was observed by keeping all other factors identical. The results are tabulated in Table 3.

Table 3: Effect of amount of N-doped SnO_2

pH = 9.5, [New Fuchsin] = 3.80×10^{-5} M, Light intensity = 40.0 $mWcm^{-2}$

N-doped SnO_2 (g)	Rate constant (k) × 10^4 (sec^{-1})
0.04	2.78
0.06	2.85
0.08	2.90
0.10	**3.37**
0.12	3.35
0.14	3.34
0.16	3.35

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 0.10 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 0.10 g, the rate of reaction becomes almost constant. After a particular value (0.10 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 new fuchsin was also observed. The results obtained are reported in Table 4.

Table 4: Effect of light intensity

pH = 9.5, [New fuchsin] = 3.80 x 10^{-5} M, N-doped SnO_2 = 0.10 g

Light intensity ($mWcm^{-2}$)	Rate constant (k) × 10^4 (sec^{-1})
20.0	1.81
30.0	2.73
40.0	**3.37**
50.0	2.62
60.0	2.49

These data indicate that photocatalytic degradation of new 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 slight decrease in the rate of reaction as the intensity of light was increased beyond 40.0 $mWcm^{-2}$.

A typical run

After keeping the values of the above parameters constant, a typical run was observed for the photocatalytical degradation of the dye. The results are shown in Table 5 and graphically presented in Figure 2. Here, a comparative observation was made for pure SnO_2 and N-doped SnO_2, which confirmed that the rate was increased almost two times in the case of N-doped SnO_2 in compare to pure SnO_2.

Table 5: A typical run

pH = 9.5, [New fuchsin] = 3.80 x 10^{-5} M, N-Doped SnO_2 = 0.10 g, Light intensity = 40.0 $mWcm^{-2}$

Time (min.)	Pure SnO_2 (Abs.)	1 + log A	N-doped SnO_2 (Abs.)	1 + log A
0	0.464	0.66	0.464	0.66
10	0.403	0.60	0.382	0.58
20	0.358	0.55	0.299	0.47
30	0.299	0.47	0.243	0.38
40	0.279	0.44	0.179	0.25
50	0.225	0.35	0.162	0.20
60	0.212	0.32	0.143	0.15
70	0.205	0.31	0.121	0.08

Rate constant (k): For pure SnO_2 = 2.05 x 10^{-4} sec^{-1}, N-doped SnO_2 = 3.37 x 10^{-4} sec^{-1}

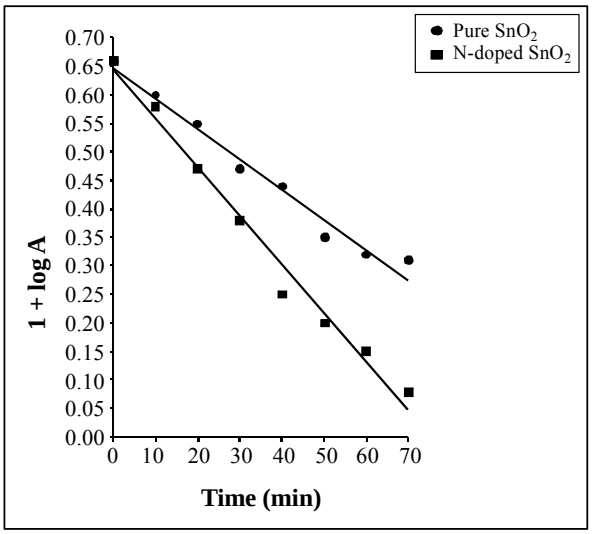

Fig. 2: A typical run

Mechanism

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

New Fuchsin (NF) 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. The participation of $^{\bullet}OH$ radical as an active oxidizing species was confirmed by using hydroxyl radical scavenger (2-propanol), where the rate of degradation was drastically reduced.

$$^{1}NF_0 \xrightarrow{hv} {}^{1}NF_1 \quad \ldots(1)$$

$$^{1}NF_1 \xrightarrow{ISC} {}^{3}NF_1 \quad \ldots(2)$$

$$SC \xrightarrow{hv} e^{-}(CB) + h^{+}(VB) \quad \ldots(3)$$

$$h^{+} + {}^{-}OH \longrightarrow {}^{\bullet}OH \quad \ldots(4)$$

$$^{\bullet}OH + {}^{3}NF_1 \longrightarrow \text{Products} \quad \ldots(5)$$

CONCLUSION

Nitrogen doped tin oxide was prepared by precipitation method by doping pure SnO_2 with urea. Different rate affecting parameters like pH, dye concentrations, catalyst amount and light intensity were studied for the dye degradation. The observations revealed that new fuchsin dye was degraded successfully by using N-doped SnO_2 under visible light. In comparative study, it was found that the N-doped SnO_2 has shown two times enhanced photocatalytic activity than pure SnO_2 and it will explore its use for degradation of many more pollutants.

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