



Research Paper

Photocatalytic degradation of safranine O in the presence of nickel oxide

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Abstract - Now a days, nature is suffering from a serious problem of environmental pollution. Industrial effluents are major sources causing water pollution. In the last two decades photocatalysis has been attracted the attention of scientific community all over the world. The present work is, on the photocatalytic behaviour of nickel oxide on safranine O. The progress of the reaction has been monitored spectrophotometrically. The influence of pH, amount of semiconductor, dye concentration and light intensity were thoroughly investigated and well regulated. The photodegradation reactions were conducted in basic medium and over the room temperature. The present study suggests that semiconductor might have played an important role in the degradation of dyes through their photocatalytic reactions. The tentative mechanism of photocatalytic reaction has been discussed.

Key words: Safranine O, Nickel oxide, Photocatalytic degradation etc.

Introduction

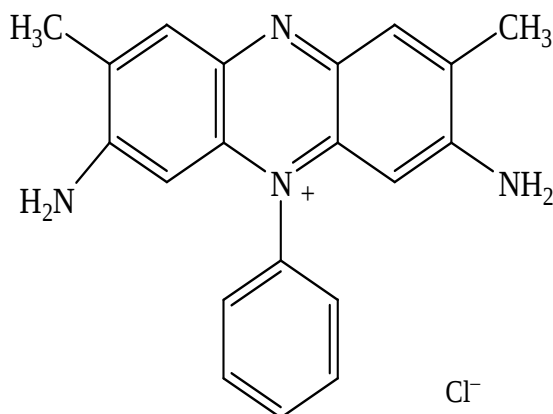
The removal of dyes from water has drawn the attention of scientists and a lot of work has been carried out in this field. TiO_2 has been frequently used as a semiconductor for this purpose^[1-4]. The enhanced photocatalytic activities of Ta co-doped TiO_2 thin films under visible light has been reported by Obata et al.^[5] while Zou and Ye^[6] used visible light sensitive photocatalyst In 1- XMXTaO_4 . Oxygen evolution on a tantalum oxynitride photocatalyst under visible light irradiation has been observed by Nakamura et al.^[7]. They also reported photo-oxidation on a metal oxynitride surface. A novel preparation of the three dimensionally macroporous M/Ti (M-Zr or Ta) mixed oxide nanoparticles with enhanced photocatalytic activity has been suggested by Wang et al.^[8].

Safranine O is a biological stain used in cytology. Safranine O is used as a counterstain in some staining protocols, colouring all cell nuclei red. It can also be used for the detection of cartilage^[9] mucin and mast cell granules. Safranines are the azonium compounds of symmetrical 2, 8-dimethyl-3, 7-diamino-phenazine. They are obtained by the joint oxidation of one molecule of a para-diamine with two molecules of a primary amine.

Safranine O is heterocyclic azine group of dyes, which is a derivative of phenazine. Nickel oxide is successfully used as a photocatalyst because of its non-

toxicity, photochemical stability, low cost, ready availability, greater efficiency and convenient way of treating several dye pollutants. Recent efforts have been focused at exploring means to utilize effectively the cheaper visible light sources or to use a greater quantity of the inexhaustible visible light for treating polluted eco systems.

Safranine O is a basic dye. Its molecular formula is $\text{C}_{20}\text{H}_{19}\text{ClN}_4$ and molar mass is 350.85 g/mol. The structure of safranine O is shown below:



Dyestuffs represent a class of organic pollutants that absorb visible light. Semiconductor powders have been used as photocatalyst to drive a particular reaction in a desired direction. TiO_2 -mediated photocatalysis has been successfully used to degrade pollutant.^[10-14]

Material and Methods

Safranin O (Sigma) and nickel oxide (Qualigens) were used in present investigations.

Apparatus

Spectrophotometer (Systronics Model-104), solarimeter (CEL Model-SM 201) and digital pH meter (Systronics Model-371) were used for the measurement of absorbance, light intensity and pH, respectively.

0.3508 g safranin O was dissolved in 500 mL doubly distilled water so that the concentration of dye solution was 1.00×10^{-3} M. It was used as a stock solution. This solution was further diluted.

The optical density of this dye solution was determined with the help of spectrophotometer at $\lambda_{\text{max}} = 515$ nm. This dye solution was placed in equal amounts (50.0 mL) in four beakers.

- (1) The first beaker containing safranin O solution was kept in dark.
- (2) The second beaker containing safranin O solution was exposed to light.
- (3) The third beaker containing safranin O solution and 0.50 g NiO was kept in dark, and
- (4) The fourth beaker containing safranin O solution and 0.50 g NiO was exposed to light.

After keeping these beakers for 4 hours, the optical density of the solution in each beaker was measured with the help of a spectrophotometer. It was found that the solutions of first three beakers had almost the same optical density while the solution of fourth beaker had a decrease in its initial value of optical density. From this observation, it becomes clear that this reaction requires presence of both; the light as well as semiconductor NiO. Hence, this reaction is photocatalytic in nature.

50.0 mL of 4.0×10^{-6} M of safranin O was taken in a beaker and 0.50 g of NiO was added to it. The pH of the reaction mixture was adjusted to 11.0. Then the solution was exposed to a 200 W tungsten lamp and aliquot of 2.0 mL was taken out from the reaction mixture at regular time intervals and its optical density was observed at 515 nm.

It was observed that the concentration of safranin O decreases with increasing time of exposure. A plot of $1 + \log \text{O.D.}$ against time was found to be linear. The rate constant was measured with the expression- $k = 2.303 \times \text{slope}$.

Results and Discussion

Typical Run

The plot of $1 + \log \text{O.D.}$ and time was found to be linear and hence, the reaction followed pseudo-first order kinetics shown in Table 1 and graphically represented in Figure 1.

Effect of pH

The photochemical reaction between nickel oxide and safranin O may be affected by pH and therefore, the effect of pH on this photochemical reaction has been investigated in the pH range 9.0 to 12.0 keeping all other factors identical. The results are shown in Table 2.

It is evident from above data that the rate of photocatalytic degradation of safranin O increases with increase in pH. The increase in rate of photocatalytic degradation may be due to more availability of the OH^- at higher pH values. OH^- will generate more $\bullet\text{OH}$ by combining with the hole and these hydroxyl radicals are responsible for this photocatalytic degradation. As the pH of the solution was increased, more OH^- will be available and these will be adsorbed on the surface of the semiconductor making it negatively charged and as a consequence of repulsive force between two negatively charged species (OH^- and electron rich dye). The approach of electron rich safranin O to the semiconductor surface will be retarded. This will result into a decrease in the rate of photocatalytic degradation of safranin O.

Effect of Concentration of Safranin O

Effect of variation of dye concentration was studied by taking different concentrations of safranin O. The results are tabulated in Table 3.

It has been observed that the rate of photocatalytic degradation increases with an increase in the concentration of the dye upto 4.0×10^{-6} M. It may be due to the fact that as the concentration of the safranin O was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye starts acting as a filter for the incident light and it does not permit the desired light intensity to reach the semiconductor surface; thus, decreasing the rate of photocatalytic degradation of safranin O.

Effect of Amount of Semiconductor

The amount of semiconductor may also effect the rate of photocatalytic degradation of safranin O and therefore, the amount of semiconductor was varied from 0.35 g to 0.65 g keeping all the other factors identical. The result are tabulated in Table 4.

As indicated from the data, an increase in the amount of semiconductor also increases the rate of photocatalytic reaction up to a certain amount of semiconductor (saturation point). This can be explained on the basis that with an increase in the amount of semiconductor, the surface area of the semiconductor will increase and hence, the increase in the rate of reaction. But after a certain limiting amount of semiconductor; if the amount of semiconductor is further increased, then it will not contribute to an increase in the exposed surface area. On the contrary, it will increase only the thickness of the layer of semiconductor powder at the bottom of the reaction vessel and thus, the saturation point is reached.

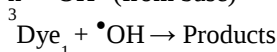
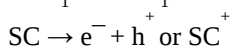
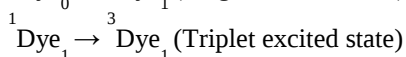
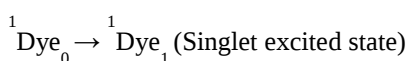
Effect of Light Intensity

The effect of the variation of the light intensity on the rate was also investigated and the observations are reported in Table 5.

The data indicate that the bleaching action is accelerated as the intensity of light was increased, because any increase in light intensity increases the number of photons striking per unit area of the semiconductor. A linear behaviour between light intensity and the rate of reaction was observed. However, higher intensities were avoided due to thermal effects.

Mechanism

On the basis of above studies, a tentative mechanism has been proposed for the bleaching of dye by nickel oxide semiconductor.



Dye absorbs the light and gets excited to its first singlet state. This gets converted to triplet state through intersystem crossing. On the other hand, the semiconductor gets excited by absorbing light and an electron is excited from its valence band to conduction band leaving behind a hole. This hole abstracts an electron from OH⁻ ions generating $\bullet\text{OH}$ free radical. The dye is bleached by this $\bullet\text{OH}$ radical. The participation of $\bullet\text{OH}$ radical was confirmed by using scavenger (2-propanol), which almost stops the degradation.

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Table 1. A Typical Run

[Safranine O] = 4.0×10^{-6} M;
pH=11.0;

Light intensity = 47.0 mW cm^{-2} ;
NiO = 0.50 g;

Time (Min.)	Optical Density (O. D.)	1 + log O.D.
0.0	0.894	0.9510
15.0	0.661	0.8200
30.0	0.502	0.7000
45.0	0.366	0.5630
60.0	0.263	0.4190
75.0	0.194	0.2870

$$k = 2.55 \times 10^{-4} (\text{sec}^{-1})$$

Table 2. Effect of pH

[Safranine O] = 4.0×10^{-6} M;
Light intensity = 47.0 mW cm^{-2} ;

NiO = 0.50 g;

pH	$k \times 10^4 (\text{sec}^{-1})$
9.0	1.60
9.5	1.94
10.0	2.12
10.5	2.30
11.0	2.55
11.5	2.35
12.0	1.89

Table 3. Effect of concentration of Safranine O

NiO = 0.50 g;
pH = 11.0;

Light intensity = 47.0 mW cm^{-2} ;

[Safranine O] $\times 10^6$ M	$k \times 10^4 (\text{sec}^{-1})$
2.8	1.33
3.2	1.81
3.6	2.21
4.0	2.55
4.4	1.84
4.8	1.53
5.2	1.30

Table 4. Effect of amount of semiconductor

[Safranine O] = 4.0×10^{-6} M;
pH = 11.0;

Light intensity = 47.0 mW cm^{-2} ;

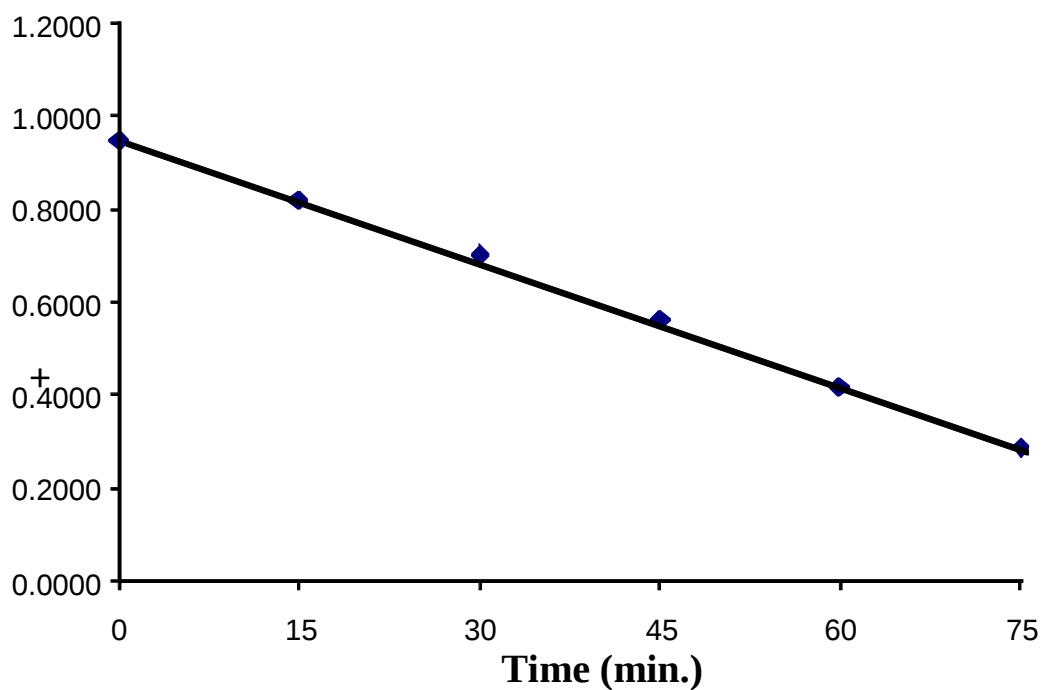
Amount of semiconductor (g)	$k \times 10^4 (\text{sec}^{-1})$
0.35	1.78
0.40	2.08
0.45	2.33
0.50	2.55
0.55	2.52
0.60	2.52
0.65	2.52

Table 5. Effect of light intensity

[Safranin O] = 4.0×10^{-6} M;
pH = 11.0;

NiO = 0.50 g;

Light intensity (mW cm^{-2})	$k \times 10^4 (\text{sec}^{-1})$
29.0	1.02
32.0	1.10
35.0	1.16
38.0	1.38
41.0	1.74
44.0	2.20
47.0	2.55

**Figure 1. Photocatalytic Degradation of Safranin O.**