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ROLE OF FERRIC TUNGSTATE AS PHOTOCATALYST FOR REMOVAL OF XYLENOL ORANGE

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ABSTRACT

In the present work, semiconducting ferric tungstate powder has been used as a photocatalyst for the degradation of xylenol orange. The photocatalyst has been prepared by precipitation method. The degradation process of the dye was monitored spectrophotometrically. Various factors, which affect the rate of reaction including pH, dye concentration, amount of semiconductor, light intensity, etc. has been studied. The observations revealed that the degradation of xylenol orange followed pseudo-first order kinetics. A tentative mechanism for photocatalytic degradation of xylenol orange has also been proposed where the species superoxide anion radical ($O_2^{-\bullet}$) was found responsible for the degradation of the dye.

Key words: Photocatalytic degradation, Ferric tungstate, Xylenol orange, Superoxide anion radical.

INTRODUCTION

The entire world is facing the problem of water pollution and a search is still on for the treatment of effluents of various industries. Majority of industrial houses do not give priority to the treatment of their effluents or to recycle the water. Many methods have been tried for the treatment of waste water like adsorption, flocculation, biological, oxidation but these methods have their own demerits along with their advantages. Photocatalysis is an emerging technology and has been used for the degradation of organic pollutants in industrial effluents.

Various binary, ternary and modified semiconductors have been successfully used for removal of a number of organic pollutants. Juang et al.[1] examined photodegradation and mineralization of single and binary acid orange 7 and reactive red 2 under UV irradiation in TiO_2 suspensions while Byrappa et al.[2] reported sunlight mediated photocatalytic degradation of rhodamine B dye using hydrothermally prepared ZnO. Bromophenol blue, crystal violet and reactive red dyes were successfully photoreduced using ZnS nanoparticles after 3.0 h of irradiation by Sharma et al.[3] where as Warrier et al.[4] have reported that CdS and CdSe nanoparticles can act as very efficient and highly chemoselective photocatalysts for the reduction of aromatic azides to aromatic amines.

Sharma et al.[5] used zinc sulphide semiconductor as a photocatalyst for the removal of rose bengal dye. Ameta et al.[6] synthesized cerium iron oxide catalyst using co-precipitation method and specific heating

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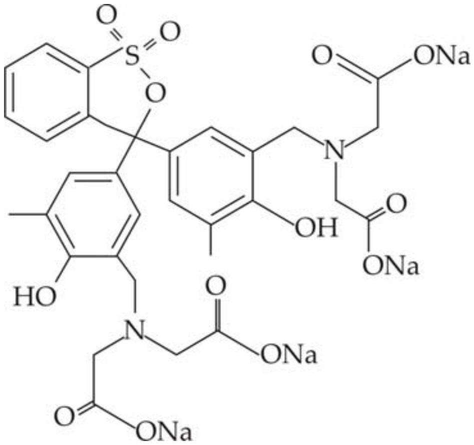
cycles. Photocatalytic degradation of alizarin red dye was observed using this catalyst and progress of the reaction was monitored spectrophotometrically while Wu et al.[7] prepared uniform colloidal Bi_2S_3 nanodots and nanorods with different sizes in a controllable manner via a hot injection method. All the prepared Bi_2S_3 nanostructures showed high efficiency in the photodegradation of rhodamine B. Bhati et al.[8] prepared nanosized bimetal ternary oxide ($CeNiO_3$) ultrafine powder using microwave heating. It has been characterized by XRD and SEM and the photocatalytic activity has been examined using the degradation of fast green dye as the model system where as Kaur et al.[9] synthesized La_2CoO_4 by a fast and simple microwave method using lanthanum nitrate and cobalt nitrate as starting reagents. The photocatalytic behaviour of La_2CoO_4 was studied spectrophotometrically through bleaching of azure-B and yellowish orange dyes.

Sharma et al.[10] carried out photocatalytic degradation of azure-B using Well-Dawson Polyoxometalate. The photocatalytic behaviour of the prepared iron containing Well-Dawson polyoxometalate was tested through the degradation of this dye. Song et al.[11] synthesized $ZnWO_4$ nanorods doped with cadmium ions successfully by a hydrothermal crystallization process. The results of the photocatalytic degradation of rhodamine B in aqueous solution showed that cadmium ions doping also greatly improved the photocatalytic efficiency of $ZnWO_4$ nanorods. Ameta et al.[12,13] have carried out photocatalytic degradation of azure B and methylene blue dye successfully using Well-dowson polyoxometalate and ferric tungstate, respectively.

EXPERIMENTAL

Xylenol orange dye used was purchased from s d fine-Chem. It is an organic reagent, most commonly used as a tetrasodium salt as an indicator for metal titrations. The structure of the dye is given below.



Structure of xylenol orange

The IUPAC name of the dye is 3,3′-Bis[N,N-bis(carboxymethyl)aminomethyl]-o-cresol sulfonephthalein tetrasodium salt. Its shows maximum absorbance at 570 nm. Doubly distilled water was used for the preparation of all solutions. Ferric tungstate [$Fe_2(WO_4)_3$] was prepared by precipitation method.

A 200 W tungsten lamp (Phillips) was used for irradiating the solution in the visible range. The intensity of light was measured with the help of Solarimeter Surya Mapi (Model CEL 201) in units of $mWcm^{-2}$. The pH of the solutions were measured by a digital pH meter (Systronics Model 335). The desired pH of solution was adjusted by addition of previously standardized sulphuric acid and sodium hydroxide solutions. Visible spectrophotometer (Systronics Model 106) was used for measuring optical density at different time intervals.

0.0761 g of xylenol orange was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. This stock solution was further diluted. The optical density of xylenol orange solution was determined with the help of a spectrophotometer at λ_{max} = 570 nm. The dye solution was placed in equal amounts in four beakers.

- The first beaker containing xylenol orange solution was kept in dark.
- The second beaker containing xylenol orange solution was exposed to light.
- The third beaker containing xylenol orange solution and 0.10 g ferric tungstate was kept in dark, and
- The fourth beaker containing xylenol orange solution and 0.10 g ferric tungstate was exposed to light.

After keeping these beakers for 3-4 hours, the optical density of the solution in each beaker was measured with the help of a spectrophotometer. It was found that the optical density of solutions of first three beakers remained almost constant, while the solution of fourth beaker had a decrease in initial value of optical density. From this observation, it is clear that this reaction requires presence of both; the light as well as semiconductor ferric tungstate. Hence, this reaction is a photocatalytic reaction in nature.

A solution of 2.00×10^{-5} M xylenol orange was prepared in doubly distilled water and 0.10 g of ferric tungstate was added to it. The pH of the reaction mixture was adjusted to 8.0 and then this solution was exposed to a 200 W tungsten lamp at 70.0 mWcm^{-2}. A decrease in optical density of xylenol orange solution was observed with increasing time of exposure. A plot of 1 + log O.D. against time was found to be linear, which indicates that the photocatalytic degradation of xylenol orange follows pseudo- first order kinetics. The rate constant was measured with the help of equation: Rate constant (k) = 2.303 × Slope

RESULTS AND DISCUSSION

A typical run has been presented in Table 1 and graphically represented in Fig. 1.

Table 1: A typical run

pH = 8.0 Ferric Tungstate = 0.10 g Light
[Xylenol Orange] = 2.00×10^{-5} M Intensity = 70.0 mWcm^{-2}

Time	Optical Density (O.D.)	1+ log O.D.
0.0	0.609	0.7846
20.0	0.588	0.7694
40.0	0.575	0.7597
60.0	0.561	0.7490
80.0	0.533	0.7267
100.0	0.518	0.7143
120.0	0.513	0.7101
140.0	0.495	0.6946
160.0	0.478	0.6794
180.0	0.464	0.6665
		k = 2.47×10^{-5} sec^{-1}

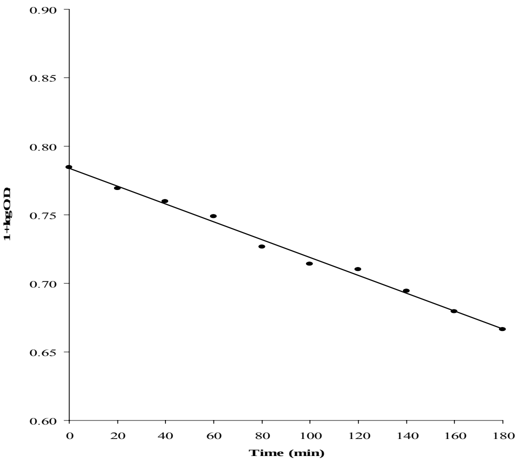


Fig. 1: Typical run

Effect of pH

The pH of the solution may affect degradation rate of xylenol orange and hence, the effect of pH on photocatalytic degradation of xylenol orange was investigated in the pH range 6.0-9.5. The results are reported in Table 2 and graphically presented in Fig. 2. It has been observed that the rate of photocatalytic degradation of xylenol orange increases with increase in pH upto 8.0. A further increase in pH above 8.0 results in a decrease in the rate of reaction.

This behavior may be explained on the basis that the rate of photocatalytic degradation increases as pH was increased because there was greater probability for the formation of oxygen anion radicals ($O_2^{-\bullet}$), which are produced from the reaction between O_2 molecule and electron (e^-) of the semiconductor. Thus, the rate of photocatalytic degradation of the dye increases. On further increase in pH above 8.0, a decrease in the rate of photocatalytic degradation of the dye may be due to the fact that xylenol orange will remain in its anionic form and experience a force of repulsion with negatively charged surface of the semiconductor (due to adsorption of more ^-OH ions on the surface of photocatalyst).

Table 2: Effect of pH

[Xylenol orange] = 2.00×10^{-5} M Light intensity = 70.0 $mWcm^{-2}$
Ferric tungstate = 0.10 g

pH	**k × 10^5 (sec^{-1})**
6.0	0.84
6.5	1.05
7.0	1.34
7.5	1.88
8.0	**2.47**
8.5	1.79
9.0	1.15
9.5	0.82

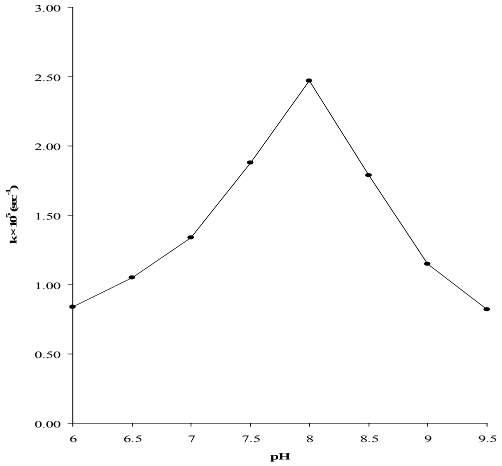


Fig. 2: Effect of pH

Effect of dye concentration

Effect of variation of dye concentration was also observed by taking different concentrations of xylenol orange. The results are tabulated in Table 3 and graphically represented in Fig. 3.

It is evident from the data that the rate of photocatalytic degradation of dye increases with an increase in concentration of the xylenol orange. It may be explained on the basis that as the concentration of the dye was increased, more dye molecules were available for excitation and consecutive energy transfer and hence, an increase in the rate of photocatalytic degradation of the dye was observed. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye above 2.00 × 10^{-5} M. It may be due to the fact that after this concentration, the dye will start acting as an internal filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles. As a result, the degradation rate decreases.

Table 3: Effect of xylenol orange concentration

pH = 8.0 Light Intensity =70.0 mWcm^{-2}
Ferric Tungstate = 0.10 g

[Xylenol Orange] × 10^5 M	k × 10^5 (sec^{-1})
1.20	0.86
1.40	1.11
1.60	1.38
1.80	2.04
2.00	**2.47**
2.20	1.92
2.40	1.38
2.60	0.88
2.80	0.53

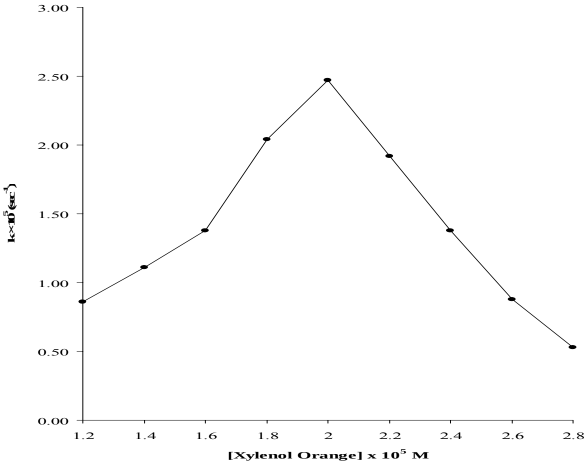


Fig. 3: Effect of dye concentration

Effect of amount of semiconductor

The amount of semiconductor may also affect the rate of degradation of xylenol orange and hence, different amounts of photocatalyst were used. The results are reported in Table 4 and graphically presented in Fig. 4. It has been observed that the rate of photocatalytic degradation of xylenol orange increases on increasing the amount of semiconductor but it became virtually constant after a particular amount i.e. 0.10 g. It may be attributed to the fact that as the amount of semiconductor was increased, there was an increase in exposed surface area of the semiconductor, but after a certain limit (0.10 g), increase in the amount of semiconductor will not increase the exposed surface area.

It may be considered like a saturation point; above which there is negligible or no effect on the rate of degradation of dye, as an increase in the amount of semiconductor after this amount (0.10 g) will only increase the thickness of the layer at the bottom of the reaction vessel and not the exposed surface area. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifts to higher side for larger vessels, while reverse trend was observed for smaller vessels.

Table 4: Effect of amount of ferric tungstate

pH = 8.0	Light intensity = 70.0 $mWcm^{-2}$
[Xylenol orange] = 2.00×10^{-5} M	
Ferric tungstate (g)	**$k \times 10^5$ (sec^{-1})**
0.02	0.81
0.04	0.99
0.06	1.35
0.08	1.97
0.10	**2.47**
0.12	2.46
0.14	2.45
0.16	2.45

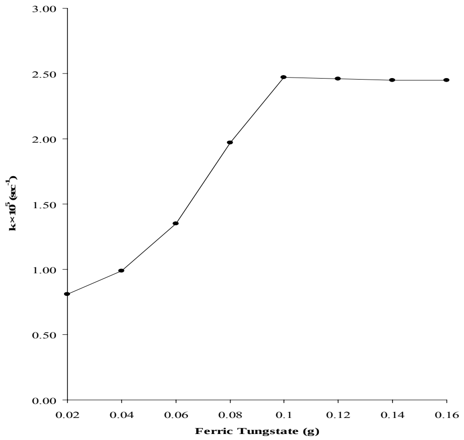


Fig. 4: Effect of ferric tungstate

Effect of light intensity

To investigate the effect of light intensity on the photocatalytic degradation of xylenol orange, the distance between the light source and the exposed surface area of photocatalyst was varied. The results are summarized in Table 5 and graphically presented in Fig. 5.

Table 5: Effect of light intensity

pH = 8.0 Ferric tngstate = 0.10 g
[Xylenol orange] = 2.00 × 10^{-5} M

Light intensity (mWcm^{-2})	k × 10^5 (sec^{-1})
20.0	0.45
30.0	0.66
40.0	0.83
50.0	1.29
60.0	1.39
70.0	**2.47**

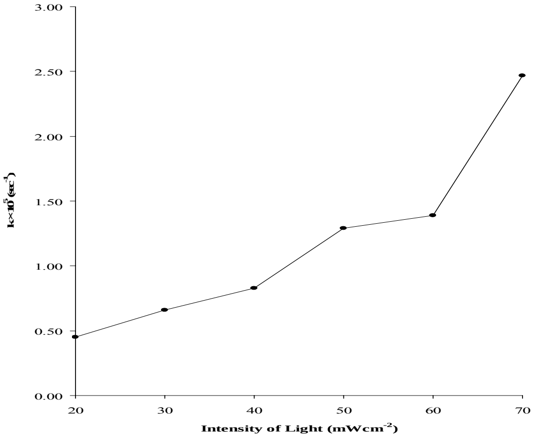


Fig. 5: Effect of light intensity

The results indicate that degradation was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder per unit time. However, on increasing the intensity above 70.0 mWcm^{-2}, there was no appreciable change in the rate of reaction.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of xylenol orange may be proposed as –

$$^{1}XO_0 \xrightarrow{h\nu} {}^{1}XO_1 \quad \text{....(1)}$$

$$^{1}XO_1 \xrightarrow{ISC} {}^{3}XO_1 \quad \text{....(2)}$$

$$SC \xrightarrow{h\nu} e^{-}(CB) + h^{+}(VB) \quad \text{....(3)}$$

$$e^{-} + O_2 \longrightarrow O_2^{-\bullet} \quad \text{....(4)}$$

$$O_2^{-\bullet} + {}^{3}XO_1 \longrightarrow \text{Leuco XO} \quad \text{....(5)}$$

$$\text{Leuco XO} \longrightarrow \text{Products} \quad \text{....(6)}$$

Xylenol orange dye (XO) absorbs radiations of suitable wavelength and gives rise to its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting ferric tungstate (SC) also utilizes the radiant energy to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will reduce the dye xylenol orange dye to its leuco form, which may ultimately degrade to products. $^{\bullet}$OH radical does not participate as an active oxidizing species in this degradation. It was also confirmed that this degradation proceeds through reduction and not oxidation as the rate of degradation was not affected appreciably in presence of hydroxyl radical scavenger (2-propanol). As a conclusion, we have reported here that the ferric tungstate has been successfully used for the photocatalytic degradation of xylenol orange.

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