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ZnO-TiO_2 Composite Mediated Photocatalytic Degradation of Orange G from Aqueous Solution

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Abstract

Composites of ZnO-TiO_2 with different ratios have been prepared by heating the mixtures at different temperatures and characterized by SEM, FT-IR and XRD techniques. The results from these techniques support the formation of the composites. These composites have been applied for photodegradation of a textile dye, orange G (OG). The composite with a composition of ZnO:TiO_2 = 75:25 prepared at 500 ^oC has been found to show the highest catalytic efficiency. The experiments have been carried out by varying the experimental conditions to optimize them. The best catalytic performance has been found with 0.25 g/100 mL of the catalyst, 1.02×10^{-4} M initial concentration of OG and the UV light source. A mechanism for photocatalytic degradation of dye has been proposed.

I. Introduction

The environment is getting polluted gradually which has become a matter of concern for most of the countries all over the world. Environmental pollution has a significant role in ecological imbalance[1]. Water pollution is one of the major classes of pollution which is mainly caused by the industrial discharge containing huge number of organic pollutants such as dyes[2-5]. The existence of these dyes in water body is quite deleterious as most of them generates toxic, non-biodegradable, carcinogenic, and/or mutagenic species after disintegration[6,7]. Moreover, coloured substances hinder light penetration through the water surface leading to disruption in photosynthetic scheme and threaten the aquatic lives[8]. Therefore, treatment of these industrial wastewater before release is essential to a great extent. Several methods have been established for handling the effluents among which advanced oxidation processes (AOPs) have procured the topmost level of attraction[9]. The basis of AOPs implies the formation of highly reactive free hydroxyl radical ($^{\bullet}OH$) that is able to oxidize organic pollutants[10]. In general, two classes of AOPs which are heterogeneous photocatalysis and homogeneous photocatalysis have been widely used for detoxification of wastewater. Heterogeneous photocatalysis has been perceived as one of the most convenient techniques for the treatment of the dyes from industrial wastes[11]. In recent decades, several investigations have been conducted using semiconductor photocatalysts for degrading dye pollutants from water[12-15]. Titanium dioxide (TiO_2) and zinc oxide are recognised as very good photocatalysts because of their high photocatalytic activities, cost effectiveness, stability, availability and non-toxic nature[16-18]. The bandgap of these two metal oxides are almost similar which is ~3.2 eV. Wide band gap leads to the limited light response as it can absorb only within the UV region.[19,20] Moreover, rapid electron-hole pair recombination has an adverse effect on photocatalysis using ZnO and TiO_2 due to low competence for photon-to-electron transformation[21,22].

In order to overcome these problems, different methods have been explored, such as doping of metals and non-metals onto TiO_2 or ZnO, and coupling of two or more semiconducting oxides. The latter method is considered to be the most effective technology to achieve efficient separation of photon induced electron-hole pairs and to improve the photocatalytic efficiency of the catalysts[23,24]. The rate of recombination of electron-hole pair is minimized by the coupling of ZnO and TiO_2 and thus improved photocatalytic efficacy can be obtained. Until recently preparation of ZnO:TiO_2 composite photocatalysts has been carried out by thermal evaporation[25], co-precipitation method[26], solid-state synthesis[27], sol-gel method[28] etc. In this present study, ZnO:TiO_2 composite photocatalyst of different molar ratios has been prepared using solid-state synthesis method and characterized by different techniques such as scanning electron microscopy (SEM), FT-IR spectroscopy and X-ray diffractometry (XRD). An anionic textile dye, orange G (OG, Fig.1) has been utilized to test the photocatalytic activity of the synthesized composite in the presence of different light sources which are visible light, sunlight and UV radiation. The efficiency of the prepared materials will be compared with that of the individual component.

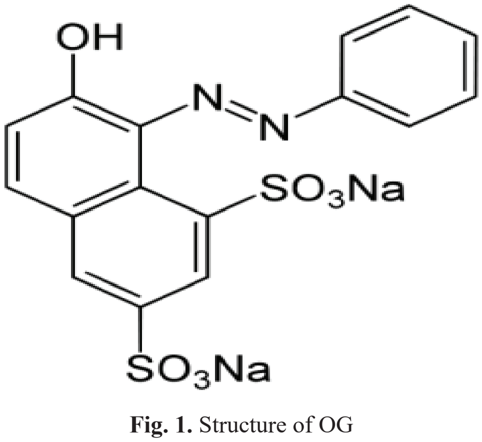

Fig. 1. Structure of OG

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II. Experimental

Materials

ZnO and TiO$_2$ were obtained from Sigma-Aldrich and used here for preparation of ZnO-TiO$_2$ composites. The OG was purchased from BDH, England. All these chemicals have been used without any further treatment.

Preparation of ZnO-TiO$_2$ composite photocatalysts

The composites were prepared in various ratios which are ZnO:TiO$_2$ 90:10, 75:25, 60:40, 45:55, 30:70 and 15:85. To prepare a composite of a particular ratio, required amounts of ZnO and TiO$_2$ were taken in a grinder and ground together in a mortar. Then solid-state reaction is being carried out in muffle furnace for 3 hours at different temperatures. Similarly, only pure ZnO and TiO$_2$ were also treated separately in the muffle furnace under the same conditions to compare the removal efficiency of the composite with these bare oxides.

Characterization of the prepared ZnO-TiO$_2$ composite

The morphology of the prepared composite was visualised by SEM. The FT-IR spectrophotometer was used for characterization at the molecular level and XRD was applied to analyse the composition of the phase and cell parameter of the materials.

Photocatalytic degradation of OG

In the case of photodegradation, the reaction mixture containing OG and composite suspension was irradiated by different light sources. During irradiation about 2.0 mL of reaction mixture was collected in a tube at different time intervals and centrifuged at a speed of 4000 rpm. The concentration of the supernatant solution was followed by using UV spectrophotometer by measuring the absorbance of dye at the λ_{max}. The percentage of degradation of dye has been calculated by the following equation-

$$\text{\% of degradation} = \frac{(A_0 - A)}{A_0} \times 100$$

Where, A_0 and A are initial absorbance and absorbance of dye after certain period of irradiation, respectively.

III. Results and Discussion

Characterization by SEM, FT-IR and XRD

The SEM images of the ZnO, TiO$_2$ and the prepared composite of ZnO and TiO$_2$ at a ratio of 75:25 are shown in Fig. 2. The SEM images of both ZnO and TiO$_2$ show heterogeneous surfaces. They are irregularly shaped aggregates. On the other hand, composites are composed of small agglomerates and nanoparticles. The particles of different sizes are present in the composite.

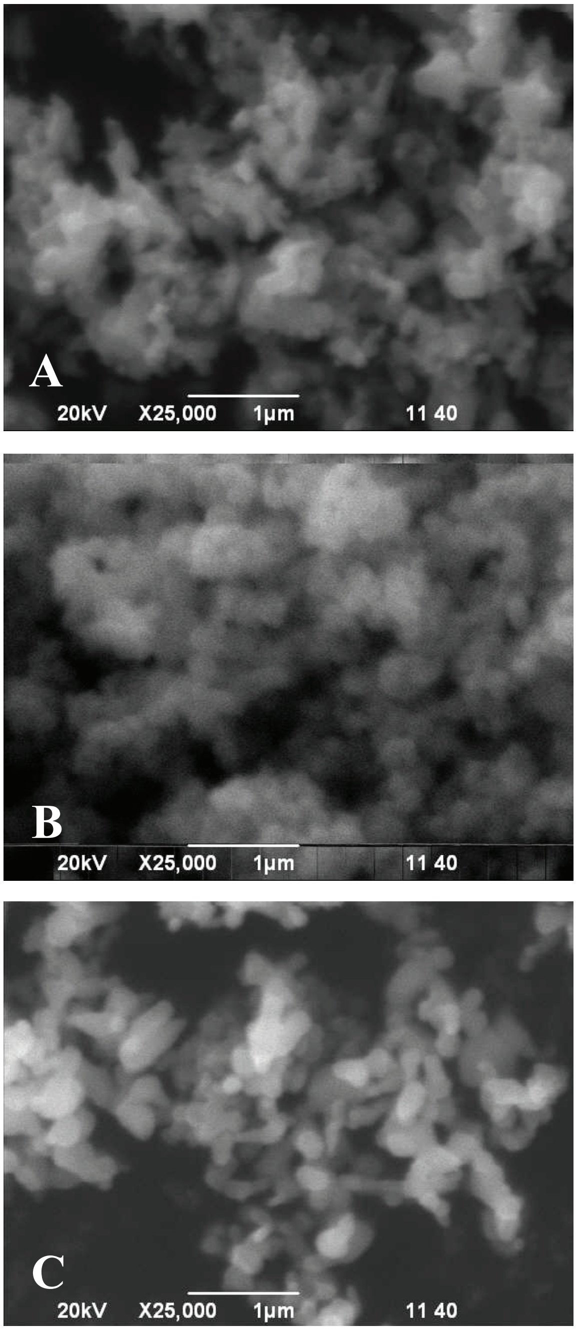

Fig. 2. SEM images of ZnO(A), TiO$_2$(B) and composite of ZnO and TiO$_2$ at a ratio of 75:25(C).

The shapes of the particles are fibrous, rod like and hexagonal. The smaller size particles with fibrous shape expectantly upgrade the surface area, which in turn stimulate the photocatalytic activity of the materials. A similar results were observed elsewhere[29].

The FT-IR spectra of ZnO, TiO$_2$ and the composite are represented in Fig. 3. FT-IR spectra were recorded by using a small amount of sample in the KBr pellet in the range of wavenumber between 4000 and 400 cm^{-1}. The peaks below

1000 cm^{-1} are due to the stretching vibrations of Zn-O and Ti-O in their respective spectra[30,31]. The composite shows the bands between 430-500 cm^{-1} which are due to the superimposition of the Zn-O stretching band of ZnO and the Ti-O stretching band of TiO_2.

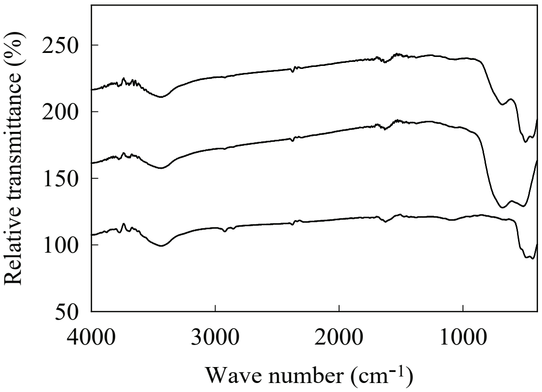

Fig. 3. FT-IR spectra of the samples: (from top) composite ($ZnO:TiO_2$=75:25), TiO_2 and ZnO. Scale of the relative transmittance was expanded to sperate the spectra.

The broad peak appearing at 3100–3600 cm^{-1} can be assigned to the fundamental stretching vibration of hydroxyl groups (free or hydrogen bonded)[32] The result is further confirmed by the appearance of a weak band at about 1620 cm^{-1}.[33] This absorption band might be caused by the intermolecular interaction of hydroxyl group of water molecule with TiO_2 surface or Ti–OH.

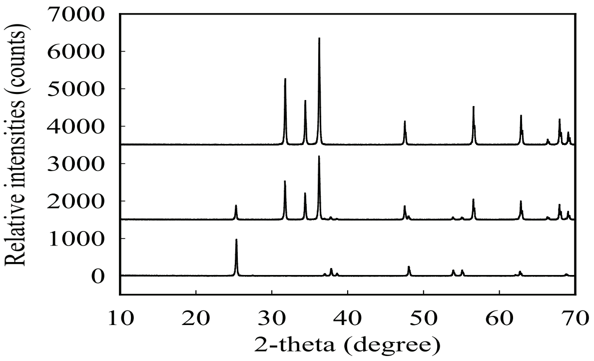

Fig. 4. XRD pattern of the samples: (from top) ZnO, composite ($ZnO:TiO_2$=75:25) and TiO_2. Scale of the relative intensity was expanded to sperate the spectra.

The XRD pattern of ZnO, TiO_2 and the prepared composite are presented in Fig. 4. A number of diffraction peaks in the XRD pattern of ZnO have been observed. These peaks appear at 2θ = 31.77°, 34.42°, 36.25°, 47.53°, 56.59°, 62.85°, 66.38°, 67.94° and 69.09° which are compatible with the planes of ZnO (100), (002), (101), (102), (110), (103), (200), (112) and (201), respectively[34,35]. These results indicate the presence of hexagonal wurtzite phase of ZnO that has been reported in JCPDS card (No. 36-1451, a = 0.3249 nm and c = 0.5206 nm). All the XRD peaks are very sharp and indicates a high degree of crystallinity of the prepared materials.

XRD pattern of TiO_2 represents a number of lines. Among them five peaks appear at 2θ = 25.34°, 36.94°, 37.80°, 38.61° and 48.04° which correspond to (101), (103), (004), (112) and (200). All these diffraction peaks are compatible with the anatase phase of TiO_2 reported in JCPDS card (No. 84-1286)[36]. The XRD pattern of the prepared composite contains several peaks. Among them the peaks at 2θ = 31.72°, 34.39°, 36.22°, 56.55°, 62.82°, 67.93° and 69.05° show that ZnO is present in the prepared composite. The diffraction peaks at 2θ = 25.28°, 37.73° and 38.53° support the presence of TiO_2 in the prepared composite. The peaks at 47.78° and 47.99° occurred because of the superimposition of the peak at 47.54° of ZnO and 48.05° of TiO_2. However, the (101) plane of ZnO and (103) plane of TiO_2 is not found in the XRD pattern of the prepared composite. It indicates that the interaction between ZnO and TiO_2 takes place at the molecular level and the prepared sample is mostly a composite of ZnO and TiO_2.

Effect of molar ratios ($ZnO:TiO_2$) of the composite on photodegradation

In order to evaluate the photocatalytic activities of the prepared composite of various molar ratios of $ZnO:TiO_2$, a set of parallel experiments have been carried out by varying the compositions which are $ZnO:TiO_2$; 00:100, 15:85, 30:70, 45:55, 60:40, 75:25, 90:10 and 100:00. The ratio 00:100 indicates TiO_2 while 100:00 indicates ZnO only. The experiments were performed by taking 0.20 g of the material of each ratio, OG concentration of 1.08×10^{-4} M under UV light irradiation (intensity = 3.31×10^{-9} Ein cm^{-3} s^{-1}). The Fig. 5a clearly represents that the composite of the ratio $ZnO:TiO_2$ = 75:25 shows the highest photocatalytic activity of 93.1% by an hour of irradiation.

When the mixture is irradiated in presence of light, electron is transferred to the conduction of TiO_2 from that of ZnO. On the other hand, the hole transfers from the valance band of TiO_2 to that of ZnO simultaneously (Fig. 5b)[37]. This is the basis of effective charge separation which promotes the life time of charge carriers as well as increases the efficacy of interfacial charge transfer to the adsorbed species. These phenomena result in accelerated photocatalytic activity of the prepared composite material. The percentage of the ZnO in the composite also influences the photocatalytic activity as adequate amount of ZnO is required to grab the photoexcited holes[38]. All other subsequent experiments were carried out by using the composite of the molar ratio, $ZnO:TiO_2$ = 75:25.

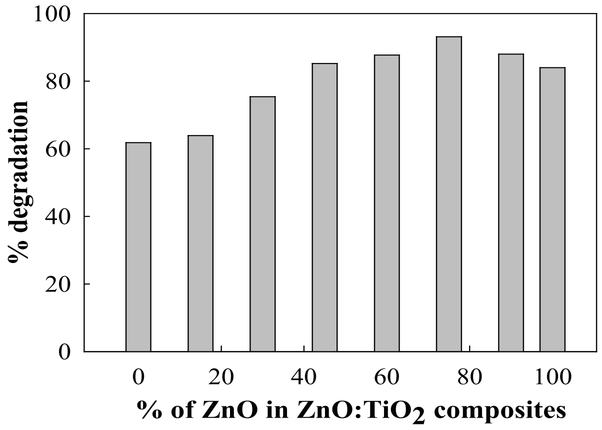

Fig. 5a. Effect of molar ratios of the components of the composite on degradation of OG. $[OG]_0=1.08\times10^{-4}$ M, amount of composite = 0.20 g, initial pH = 7.40±0.5. UV light intensity was 3.31×10^{-9} Ein cm^{-3} s^{-1} for all experiments.

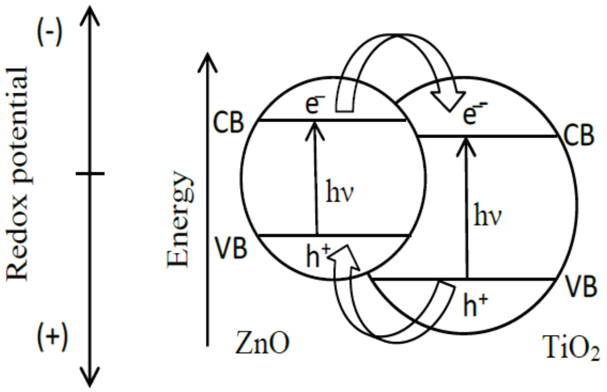

Fig. 5b. Coupling of ZnO and TiO_2 semiconductors and possible electron-hole transfer.

Effect of preparation temperatures of the composite on photodegradation

The effect of temperature, at which the composites were prepared, on the efficiency of the materials has been studied by applying these in the photodegradation experiment. The five composites were prepared by heating at 300, 400, 500, 600 and 700 °C. For each experiment 0.20 g of any one of these composites with fixing all other variables has been used. The maximum degradation was found with the composite prepared at 500˚C (Fig. 6). These experimental findings imply that with the increase in the temperature, the surface inhomogeneity may increase which ultimately increases the surface area of the composite. The composite synthesized at 500˚C works more effectively corresponding to the maximum formation of hydroxyl radical on the composite surface resulting in the destruction of the target pollutant. Moreover, maximum degradation achieved at this temperature was contributed by the formation of higher anatase phase[39]. The decrease in the photocatalytic activity for the composites prepared at higher temperatures can be explained by the fact that the particles can agglomerate to form larger particles. This might cause a decrease in the surface area.

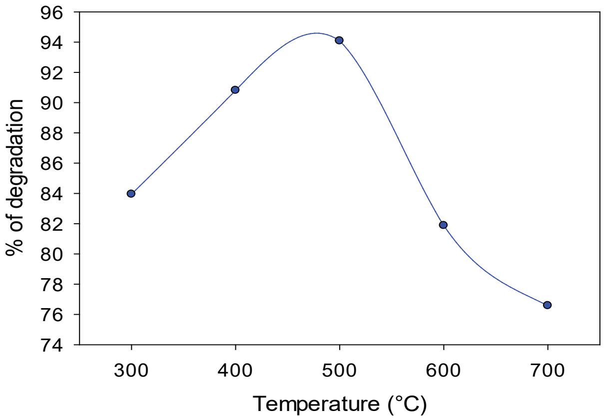

Fig. 6. Effect of preparation temperatures of the composite on degradation of OG, $[OG]_0=1.02\times10^{-4}$ M, amount of composite ($ZnO:TiO_2$ = 75:25) = 0.20 g, initial pH = 7.60±0.20. UV light intensity was 3.31×10^{-9} Ein cm^{-3} s^{-1} for all experiments.

Effect of the amounts of the composite on photodegradation of OG

The percent degradation of OG increases from 72.6% to 94.1% with an increase in the amount of the material from 0.05 g to 0.20 g (Fig. 7). This can be explained by the fact that increased amount of catalyst increases the number of active sites on the catalyst surface. With a further increase in the amount of the catalyst from 0.20 g to 0.30 g, a slight decrease in the percent degradation is found. This is due to the scattering of light caused by the excessive quantity of composite particles[40]. On the contrary, higher amounts of composite cause a considerable particle aggregation which reduces the active sites on the surface of the composite. As a result, the percentage of degradation decreases. Therefore, 0.20 g of the composite has been considered as the optimum amount and used for other experiments.

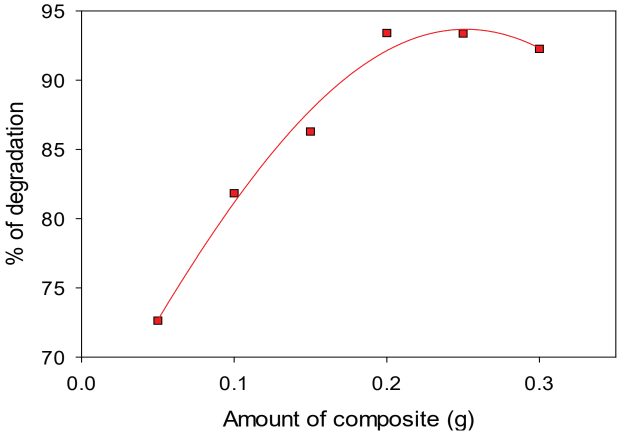

Fig. 7. Effect of amounts of composite on degradation of OG, $[OG]_0=1.02\times10^{-4}$ M, initial pH = 7.20±0.3.

Effect of OG concentrations on photodegradation

To assess the effect of the concentration of OG on photodegradation, the experiments were carried out by changing the concentrations of OG in presence of UV irradiation (Fig. 8). Descending degradation efficiency was found with an increase in the initial concentration of OG. A definite amount of composite generates a fixed number of electron-hole pairs which produce a fixed quantity of •OH radicals. The photogenerated radicals can only break down an equivalent quantity of OG. Moreover, it is obvious mathematically that the percent degradation will be lower for the high initial concentration of OG because the percent degradation is evaluated by dividing the amount of degraded dye with its high value of initial concentration. In addition, light cannot penetrate into the bulk solution due to the high concentration of the dye. Consequently, detrimental effect on the photodegradation has been found for higher concentration of the dye.

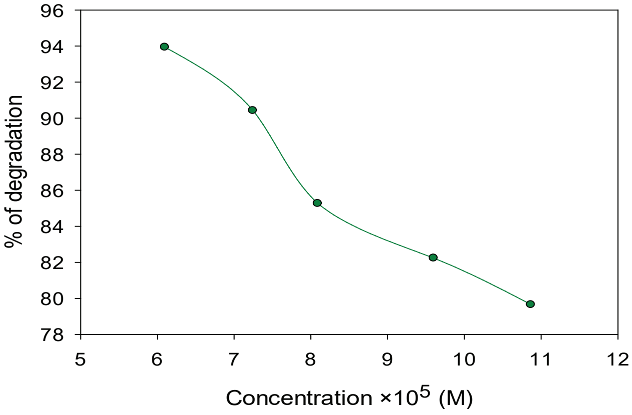

Fig. 8. Effect of initial concentrations of OG on degradation using the composite, amount of composite ($ZnO:TiO_2$ = 75:25) = 0.20 g, initial pH = 7.20±0.3.

Effect of light sources on photodegradation of OG

The effect of different light sources has been investigated using UV light, artificial visible light and sunlight (Fig. 9). The optimum concentration of OG was selected at 6.00×10^{-5} M and the mass of the composite was taken at 0.20 g. Among all the light sources, the highest percentage of degradation of OG was 93.9% which was acquired under UV light irradiation for 60 minutes. Visible light provides the lowest efficiency of degradation which is only 20.0% by the same time of irradiation. It is obvious that the number of photogenerated electron-hole pairs increases with increasing the frequency of the light photon. Hence, the visible light is less efficient than the UV light of the same intensity. Although both sun light and artificial light sources are considered as visible light source, the sun light has higher intensity than the artificial visible light.

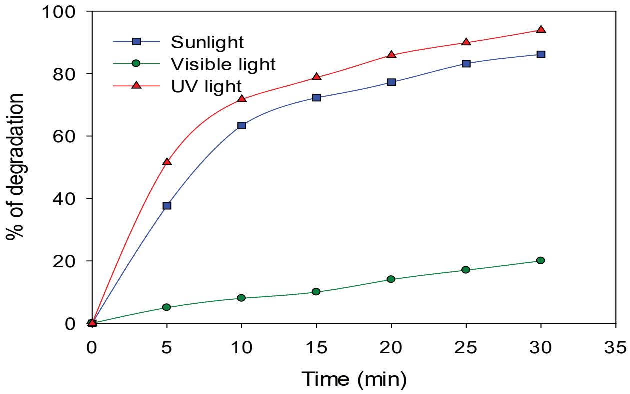

Fig. 9. Degradation of OG using the composite for different light sources, amount of composite ($ZnO:TiO_2$ = 75:25) = 0.20 g, $[OG]_0 = 6.00\times10^{-5}$ M, initial pH = 7.00±0.2.

Probable mechanism of dye degradation by ZnO-TiO$_2$ composite

The general mechanism for photodegradation of dyes under UV light by the catalyst can be summarised as following-

$$C + h\nu \rightarrow h^+ + C(e^-) \qquad (1)$$

Where C, h^+ and e^- represent composites, hole and electron, respectively. The holes and electrons can cause the following reactions.

In the presence of acid solution,

$$h^+ + (H_2O)_{ads} \rightarrow {}^\bullet OH + H^+ \qquad (2)$$

In the presence of alkali solution,

$$h^+ + OH^- \rightarrow {}^\bullet OH \qquad (3)$$

$$C(e^-) + O_2 \rightarrow C + {}^\bullet O_2^- \qquad (4)$$

$$ {}^\bullet O_2^- + H^+ \rightarrow HOO^\bullet \qquad (5)$$

$$HOO^\bullet + H^+ + C(e^-) \rightarrow H_2O_2 + C \qquad (6)$$

$$H_2O_2 \rightarrow 2\,{}^\bullet OH \qquad (7)$$

This •OH radical strikes the -N = N- linkage of the dye molecules and degrade them. Dye degradation ends up through mineralization-

$$(Dye^-)_{ads} + \text{radicals} \rightarrow \text{mineralized products}$$

In the presence of sunlight the following mechanism of photodegradation of dyes may occur.

The adsorbed dye may get excited by the adsorption of sunlight.

$$(Dye)_{ads} + h\nu_{vis} \rightarrow {}^*(Dye)_{ads} \qquad (8)$$

$$C + {}^*(Dye)_{ads} \rightarrow C(e^-) + {}^*(Dye^+)_{ads} \qquad (9)$$

$$C(e^-) + O_2 \rightarrow {}^\bullet O_2^- + C \qquad (10)$$

This $^•O_2^-$ radical can cause the reactions as (5) to (7) and generates $^•OH$ radicals as well. This $^•OH$ or other radicals decolorize and mineralize dyes.

IV. Conclusions

In this paper, we have successfully prepared thermally treated composite photocatalysts of ZnO and TiO$_2$, which show better photocatalytic efficiencies than the individual components. The surface morphology of the prepared materials have been observed by SEM and characterised by FTIR and XRD. Best photocatalytic activity has been found with a composite of ZnO:TiO$_2$ = 75:25 prepared at 500 ^{o}C. The composite has been used for efficient degradation of a textile dye, orange G from aqueous solution and the experimental variables have been optimized.

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