

Visible Light Photodegradation of Phenol Using Nanoscale TiO₂ and ZnO Impregnated with Merbromin Dye: A Mechanistic Investigation

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ABSTRACT: ZnO and TiO₂ nanoparticles were impregnated with merbromin dye and used as modified photocatalysts for degradation of phenol. Dye-modified ZnO and TiO₂ showed significantly higher photocatalytic activity than neat ZnO and TiO₂ under visible light illumination. Moreover, the prepared dye-modified ZnO showed superior photocatalytic efficiency in degradation of phenol compared to the dye-modified TiO₂. In a period of 4 hours, dye-modified ZnO removed phenol almost completely while dye-modified TiO₂ degraded it only to 47%. A cooperative working mechanism involving the possible photoactivation of both surface bound dye and semiconductor is proposed for the dye-modified systems. The suggested pathway is based on charge-transfer formalism. Furthermore, the study proposes some reasons for difference in reactivity of the dye-modified ZnO and TiO₂ catalysts. Less aggregation of dye molecules on the surface of ZnO compared to TiO₂ causes more prolonged lifetime of excited state of the dye on the surface of ZnO. Also, energy gap between the conduction band of semiconductor and LUMO level of merbromin in dye-modified ZnO is larger than dye-modified TiO₂. Both above lead to more effective electron injection from the dye to ZnO which is hypothesized to be mainly responsible for the enhancement of the reaction rate of phenol degradation.

KEY WORDS: Dye modification, Photocatalyst, TiO₂, ZnO, Phenol degradation.

INTRODUCTION

Photocatalytic reactions using TiO₂ or ZnO particles have been shown to be useful for destroying a wide range of environmental pollutants [1, 2]. The aim of researches is to achieve new catalytic systems having some advantages compared with the simply TiO₂ or ZnO catalyzed processes [3-6]. Recently, many attempts

such as doping with transition metals, transition metal ions, nonmetal atoms and sensitizing with organic materials have been made to make ZnO and TiO₂ highly reactive under visible light excitation to allow utilization of the solar spectrum [7-10].

The anchoring of pigments, on these semiconductors

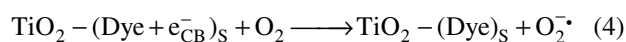
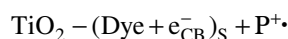
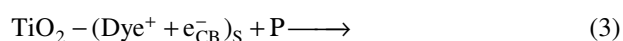
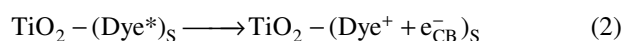
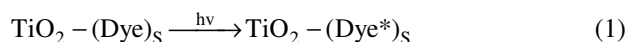
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is an alternative method to deal with this issue. According to the literatures, dye-sensitization of a photocatalyst involves activation of the surface of semiconductor photocatalyst under wavelengths longer than those corresponding to its band gap. In such a process, the surface adsorbed dye is excited by the visible light [11]. Chatterjee suggested the following mechanism for degradation of pollutant at the surface of dye-sensitized TiO₂ systems.



P= Pollutant

According to Eq. (1), illumination using visible light ($h\nu$) results in excitation of surface adsorbed dye. After that, charge injection into conduction band of the semiconductor takes place (Eq. (2)). Then pollutant reduces the oxidized surface of adsorbed dye (Eq. (3)), while electron in conduction band (e_{CB}^-) is transferred to molecular oxygen (O₂) leading to the formation of superoxide/hydroxide radicals (O₂^{•-} / HO₂[•]) in the system (Eq. (4) and (5)). It is presumed that the repeated attacks of O₂^{•-} / HO₂[•] radicals on the aromatic ring of pollutant cause the deep oxidation of aromatic involving radicaloid intermediates which, in turn, is leading to the formation of carbon dioxide as end product [12].

In this proposed mechanism, a hole is produced in the HOMO (highest occupied molecular orbit) level of the dye. This hole could oxidize the pollutants (Eq. (3)), which demand oxidizing potentials less positive than the HOMO level of the dye [13-15]. However, degradation of contaminants with more positive oxidizing potentials than the dye valence band was reported in some manuscripts [15]. The photocatalytic properties of dye-modified semiconductor photocatalysts remain

unexplored although some studies focused on dye sensitized ZnO and TiO₂.

The present work investigates phenol photodegradation efficiency at the surface of ZnO and TiO₂ particles impregnated with merbromin dye in comparison to each other. Further studies are also devised to compare the catalytic efficiency of the impregnated particles with the neat ZnO and TiO₂. The study also proposes the mechanism of photodegradation of phenol at the surface of these modified photocatalysts.

EXPERIMENTAL SECTION

Materials and apparatuses

Anatase TiO₂ nanoparticles with 25 nm average particle size was supplied by Aldrich Company. ZnO and other materials such as merbromin (C₂₀H₈Br₂HgNa₂O), phenol and ethanol were obtained from Merck Company.

Spectroscopic analysis of the matter was performed using a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer 843) and UV-Vis spectrophotometer (Shimadzu UV 2100). The morphology of the products was studied by Scanning Electron Microscopy (SEM, Philips XL30) and elemental analysis of them carried out by means of Energy Dispersive X ray Spectrometry (EDS). Powder phase identification was performed by X Ray Diffraction (XRD) obtained on Philips X-pert diffractometer using Cu-K α line ($\lambda=1.54056\text{\AA}$) radiation, working with voltage and current of 40 kV and 40 mA. Finally, the amount of Mercury ions which might be release from the dye was determined by an atomic absorption spectrometer AAS (Varian Spectra AA 200).

Preparation of the dye-modified TiO₂ and ZnO photocatalyst

TiO₂ powder was heated at 100°C for 4 hours to eliminate water adsorbed on its surface. Then 1 g of TiO₂ powder was added to a round balloon containing 50 mL of 0.1 M ethanolic solution of merbromin dye. At this stage, the pH of the mixture is about 7. After that, the mixture refluxed at 80°C for 2h to fix the dye on the surface of semiconductor particles. Then the solid fraction was filtered, washed with deionized water and 95% ethanol for three times. Finally, the particles were dried in room temperature. Dye-modified ZnO was prepared via the same method. The pH of suspension prepared from adding of ZnO powder to ethanolic solution of dye measured to be 7 as well. The dye-modified TiO₂ and ZnO turn to pink in color.

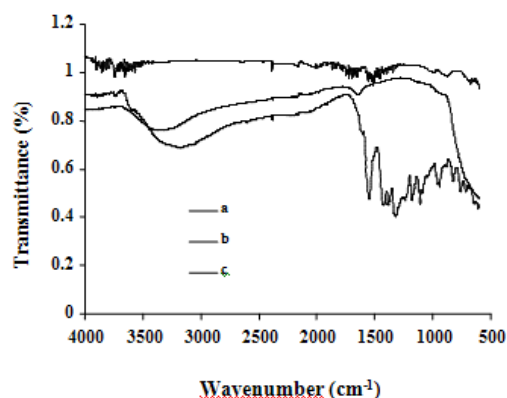


Fig. 1: FT-IR spectra of (a) merbromin modified ZnO, (b) merbromin modified TiO₂, (c) merbromin dye.

Photocatalytic experiments

All photocatalytic experiments were performed in 150 mL batch photoreactor. Visible lamp (100 W, tungsten) has been used as radiation source. The distance between the radiation source and the vessels containing reaction mixture was fixed at 12 cm, and setup was cooled with a fan. Air was continuously bubbled into the solution by an aquarium pump in order to provide a constant source of dissolved oxygen. The mixture was magnetically stirred during irradiation.

In photocatalytic experiments, 100mL aqueous solution of phenol (5 ppm) containing 0.05 g of photocatalyst was taken in the photoreactor under visible light irradiation. Decrease of phenol concentration in photocatalytic systems was monitored by measuring the absorbance of the samples via UV-Vis spectrophotometer in different intervals. Normalized absorption of phenol was followed in $\lambda=269$ nm. Furthermore, concentration of probably existent Mercury ions in the filtered solutions was determined by AAS spectrometer.

RESULTS AND DISCUSSION

Catalysts characterization

FT-IR spectra of dye-modified ZnO and TiO₂ powders and merbromin dye in transmittance mode are shown in Fig. 1.

Spectrum of merbromin is shown in curve c. The absorption peak at 1540cm^{-1} is attributed to O-C-O asymmetric stretching band of carboxyl group. The peaks $1300\text{-}1400\text{cm}^{-1}$ are due to O-C-O symmetric stretching band. The absorption of O-C-O asymmetric stretching

is observed at 1670cm^{-1} and 1610cm^{-1} for merbromin adsorbed on ZnO and TiO₂, respectively (curve a and b). As shown in spectra O-C-O stretching band at 1700cm^{-1} attributed to the ester bonding, is not observed. This indicates that merbromin molecules are adsorbed on surface of the semiconductors via carboxylate COO⁻ linkage [16]. As shown in Fig. 1 all absorption peaks of merbromin adsorbed on TiO₂ and ZnO are shifted to some extent to large wave numbers when compared to the peaks of free dye. This shift is due to the interaction between the dye molecules and semiconductor substrates.

SEM images of ZnO and TiO₂ photocatalysts particles before and after impregnating with merbromin dye are shown in Figs 2a, 2b, 3a and 3b, respectively. These images reveal nanoscale dimensions for photocatalyst particles. SEM images also show that ZnO and TiO₂ particles have been become more agglomerated after dye-modification.

EDS spectra of dye-modified ZnO and TiO₂ are presented in Figs 4a and b. Presence of Hg element in EDS spectra reveals that merbromin has been adsorbed on the surface of photocatalysts. The percentage of Hg on dye-modified TiO₂ and ZnO are 24.09% and 5.00%, respectively. The Considering to Hg percent, the amount of dye adsorption on the surface of TiO₂ is more than ZnO.

XRD patterns of ZnO and dye-modified ZnO powders are presented in Fig. 5a, and XRD patterns of nanoscale TiO₂ and dye-modified TiO₂ powders are shown in Fig. 5b. It was obviously observed that the XRD patterns of dye-modified TiO₂ and ZnO were identical with those of neat TiO₂ and ZnO. This indicates that the dye-modification of these semiconductors had no effect on the crystalline phase.

Because of spherical morphology of TiO₂ particles, the average crystallite size of the dye-modified TiO₂ can be calculated from the XRD data. According to Scherrer's equation, $D = 0.9\lambda / (\beta \cos\theta)$, where D is the average crystallite size (nm), λ is the applied X-ray wavelength ($\lambda = 1.5406 \text{ \AA}$), θ is the diffraction angle and β is a full-width at half the maximum of diffraction line observed ($2\theta = 25.3493$) in radians, the average crystallite size obtained was 32.35 nm.

Fig. 6 shows UV-Vis absorption spectra of the dye-modified ZnO and TiO₂ particles dispersed in ethanol. UV-Vis absorption spectrum of merbromin in ethanol

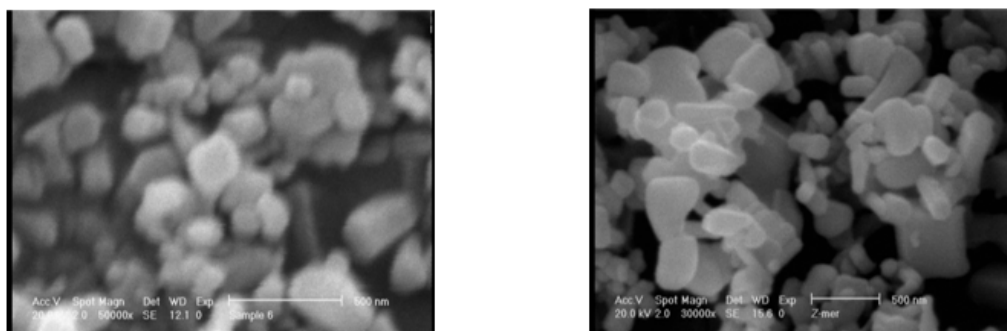


Fig. 2: SEM image of ZnO particles before and after modification.

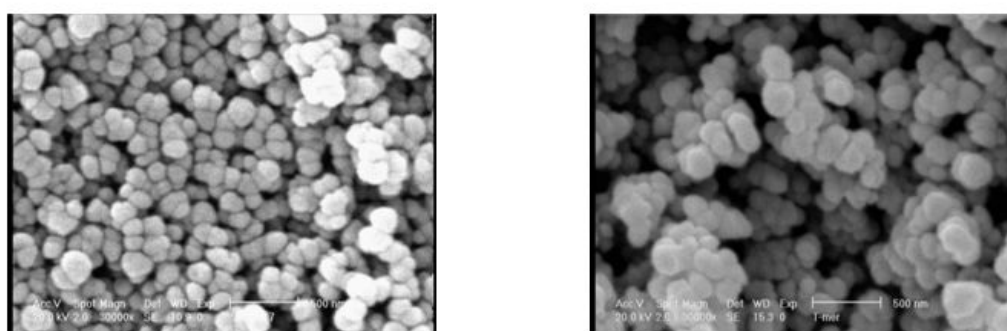


Fig. 3: SEM image of TiO₂ particles before and after modification.

(figure are not shown) has a strong absorption peak at 517 nm attributed to the absorption of the monomers and a shoulder peak at 482 nm related to the absorption of the aggregate species [17, 18]. When merbromin is absorbed by the TiO₂ and ZnO nanoparticles, the absorption peak of the monomer is observed at 523 nm due to the interaction between merbromin molecules and semiconductor particles. This result is in good agreement with that reported by Bai and coworkers [19].

Photocatalytic activity measurements

Fig. 7 shows degradation of phenol versus time during photocatalytic reaction using dye-modified ZnO nanoparticles under visible light. The inset of Fig. 7 shows the change of normalized absorption of phenol at $\lambda=269$ nm versus time at this reaction. According to Fig. 7, Phenol degradation is approximately completed during 4 hours and no leaching of merbromin dye was detected spectrophotometrically. Furthermore, AAS showed that there was no detectable Mercury ion in the filtered

solutions indicating the stable operation of merbromin in the dye-modified system.

Fig. 8 shows photocatalytic degradation of phenol versus time using dye-modified TiO₂ nanoparticles under visible light. No leaching of merbromin dye was detected spectrophotometrically and no evidence up on existence of Mercury ions was found during this photocatalytic reaction as well.

According to Fig. 8, in the first two hours of reaction period, normalized absorption (at $\lambda=269$ nm) increased temporally due to formation of some intermediates as a result of phenol destruction. These intermediates have absorption band very close to $\lambda=269$ nm. Intermediate products of phenol destruction were not identified in this study but according to the literature they are expected to be aromatic byproducts (catechol, hydroquinone, benzoquinone and resorcinol) or organic acids [20]. Formation of some intermediate species such as hydroquinone and benzoquinone, is observed with an absorption band at about 280 nm [21]. This experiment

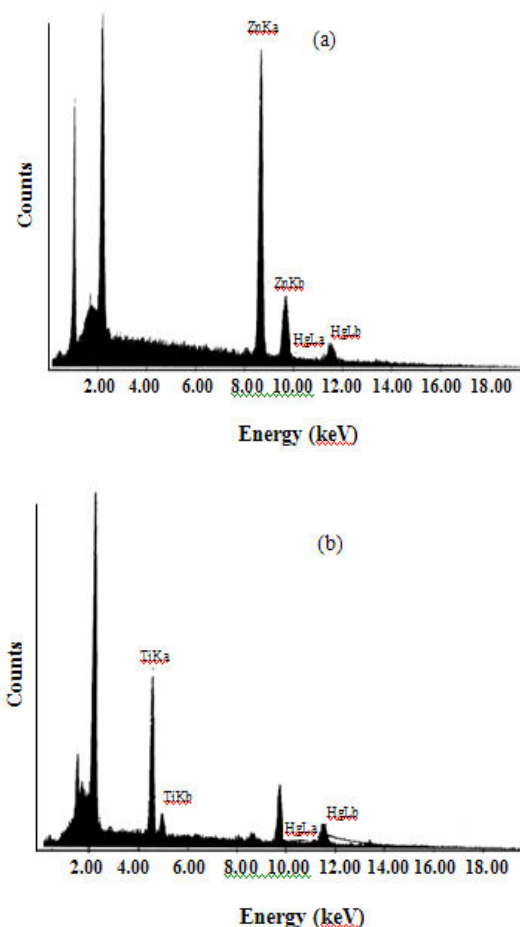


Fig. 4: EDS spectrum of (a) merbromin modified ZnO, (b) merbromin modified TiO₂.

revealed that the concentration of phenol was decreased while the concentrations of intermediates were increased in the first two hours of the reaction.

Phenol degradation rate at the surface of dye-modified ZnO is higher than that of dye-modified TiO₂. Investigations into the reasons as to why the dye-modified ZnO particles showed a higher rate of degradation of phenol may be revealing many facts. For this purpose and in order to elucidate the detailed reaction pathway of phenol depletion at the surface of dye-modified photocatalysts a series of preliminary experiments were carried out. One set was done by exposing phenol solution to visible light without the presence of catalyst (a photolysis reaction). The second and third sets were performed with phenol solution exposed to ZnO and TiO₂ without the presence of visible light (the ZnO and TiO₂ adsorption). The fourth and fifth sets were performed through exposing phenol solution

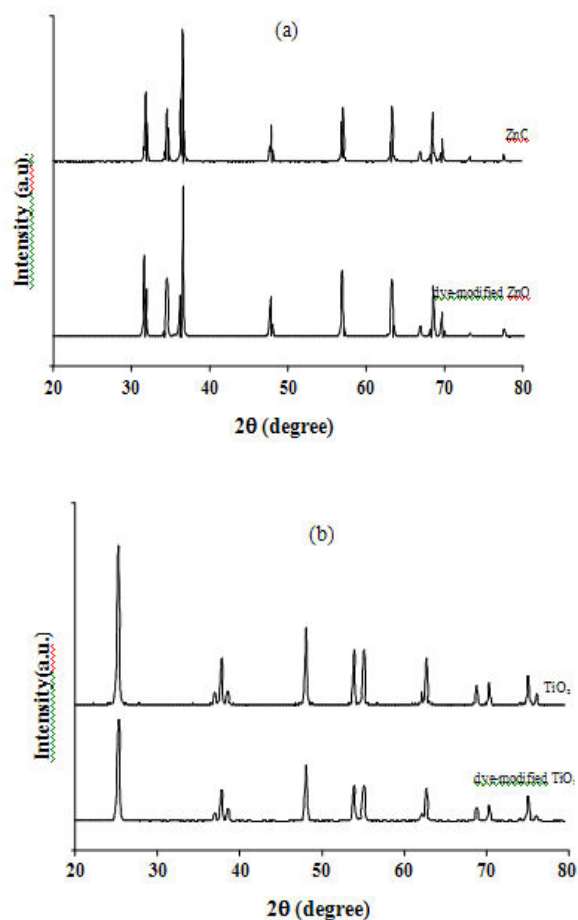


Fig. 5: XRD patterns of neat (a) ZnO and dye-modified ZnO, (b) TiO₂ and dye-modified TiO₂ nanoparticles.

to visible irradiation in the presence of neat ZnO and TiO₂ (the photocatalysis condition). The results are presented in Fig. 9.

The change of absorption spectra of phenol solution versus time in presence of neat TiO₂ nanoparticles under visible light illumination is shown in Fig. 9. The inset of Fig. 9 shows the change of normalized absorption of phenol at $\lambda=269$ nm versus time at photolysis reaction using visible light, at dark in the presence of nanoscaled ZnO and TiO₂, and under visible light in the presence of TiO₂ and ZnO particles. The photolysis reaction demonstrated that visible light alone is not able to destruct phenol structure even after 19 hours. According to inset of Fig. 9, Phenol was adsorbed on the surface of both neat catalysts in dark. However, TiO₂ adsorbed phenol molecules a bit more than ZnO. Moreover, ZnO photocatalyst could degrade phenol under visible light in 9 hours, but visible light photocatalytic degradation

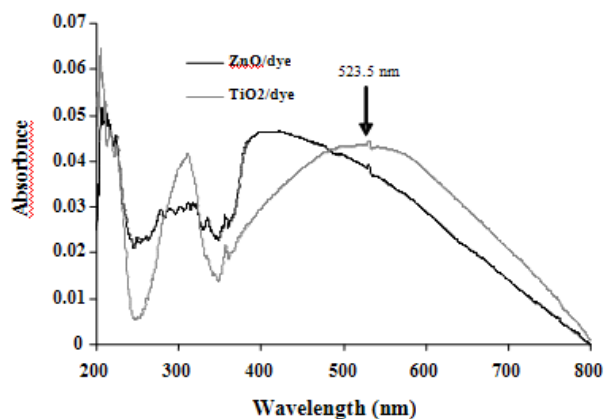
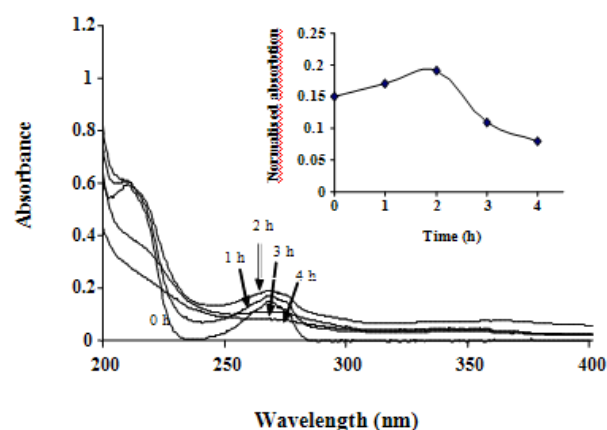


Fig. 6: UV-vis absorption spectra of the dye-modified TiO_2 and ZnO particles dispersed in ethanol.



photocatalytic reaction on dye-modified TiO_2 , inset: normalized absorption of phenol at 269 nm versus time.

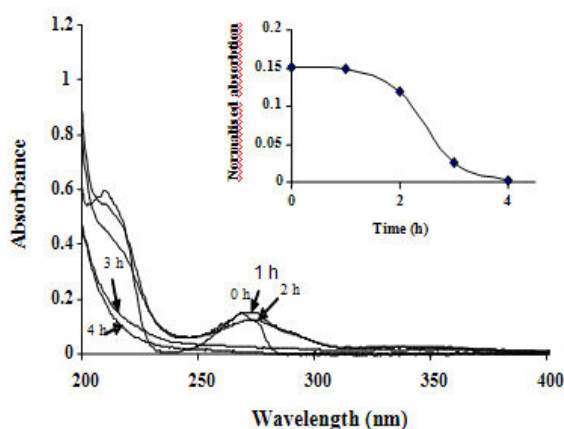


Fig. 7: UV-Vis spectra of phenol solution during visible light photocatalytic reaction on dye-modified ZnO, inset: normalized absorption of phenol at 269 nm versus time.

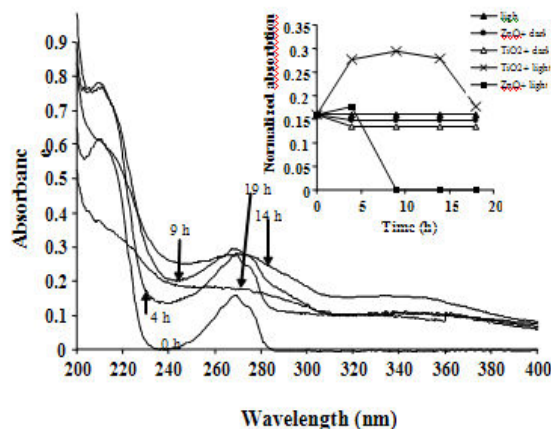


Fig. 9: Absorption spectra of phenol solution in presence of neat TiO_2 nanoparticles during visible light illumination, inset: changes of normalized absorption as a function of time at 269 nm at different condition reactions.

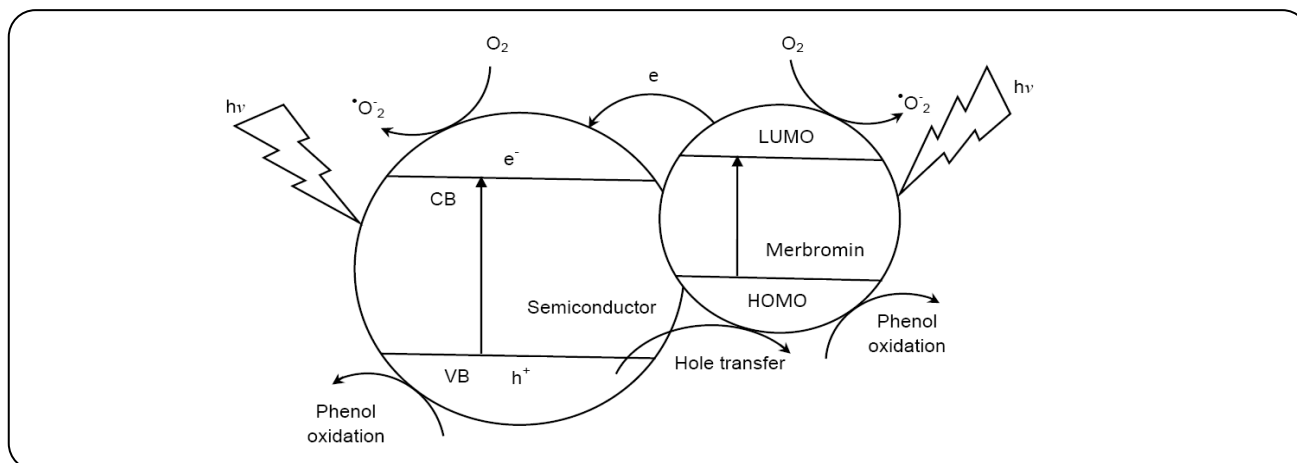
of phenol using neat TiO_2 nanoparticles could not be completed even after prolonged (19 hours) illumination. On the other hand, phenol degradation and generation of intermediates and finally conversion of intermediates to the products are done more rapidly using ZnO in comparison with TiO_2 .

Effect of merbromin dye impregnation on rate of photodegradation of phenol

Photocatalytic degradation of phenol showed that the order of efficiency in the applied photocatalyst is dye-modified ZnO > dye-modified TiO_2 > ZnO > TiO_2 . In the visible region, merbromin impregnation enhanced the catalytic activity of ZnO and TiO_2 .

The phenol photodegradation experiments using neat ZnO and TiO_2 mentioned in this work revealed that these semiconductors are themselves excited under visible light. Therefore, the ability of these semiconductor/ merbromin systems to degrade phenol in the visible region is not a sensitization process as mentioned in some literatures [12, 22]. Alternatively, the dye molecules promote the catalytic activity of ZnO and TiO_2 by other pathway. It seems that degradation of phenol in presence of dye-modified ZnO and TiO_2 is done through a cooperative mechanism, involving the possible photoactivation of both dye and semiconductor.

The photocatalytic behavior of the merbromin modified ZnO and TiO_2 could be explained regarding



Scheme 1: Schematic charge-transfer formalism in TiO₂ and ZnO nanoparticles impregnated with merbromin dye.

the position of the energy levels of the dye and semiconductors.

The HOMO level of merbromin as estimated by electrochemistry is about 0.96V (versus normal hydrogen electrode [NHE]) [23]. The energy gap between HOMO and LUMO (the lowest unoccupied molecular orbit) of merbromin is 2.37eV obtained from the absorption onset of merbromin (523nm). Hence, the LUMO level is about -1.41V (versus NHE). It is important to note that the LUMO level of the dye should be higher than the conduction band of TiO₂ and ZnO so that the injection of the photogenerated electron could be allowed from the dye to these semiconductors. It was known that the conduction band potentials of TiO₂ and ZnO are about -0.5 and -0.3V versus NHE, respectively [16]. This completely accomplishes the required condition in the dye modified-ZnO and TiO₂ systems. The intercomponent charge transfer in the dye modified semiconductor system and the occurring of the photocatalytic redox process proposed for phenol degradation on the surface of TiO₂ and ZnO impregnated with merbromin is shown in Scheme 1. When dye-modified ZnO or TiO₂ system is illuminated with visible light, both dye and semiconductor could be excited and undergo charge separation. LUMO level of the dye is more negative than conduction band of TiO₂ and ZnO semiconductors and photogenerated electrons are allowed injected from the dye to these semiconductors. So, electron injection from LUMO level of dye to conduction band of semiconductors occurs. The oxygen molecules could interact with photogenerated electrons of both LUMO level of the dye and TiO₂ or ZnO conduction

band. Hence, one reason for superior photocatalytic efficiency of dye-modified TiO₂ or ZnO compared to neat TiO₂ and ZnO could be the increasing formation of superoxide radical in these systems.

Phenol demands positive oxidation potentials more positive than 1.4 versus NHE, as calculated from thermodynamic data [15]. On the other hand, more positive potentials than 1.4 should be available to phenol oxidation occur. The needed potential for phenol oxidation is more positive than that of HOMO level of merbromin. Hence, the HOMO level of merbromin dye could not oxidize phenol. It confirms that, a sensitization mechanism of ZnO and TiO₂ by merbromin, as mentioned in some literatures [12, 22], to degrade phenol in the visible light is ruled out.

The valence band of ZnO and TiO₂ are significantly more positive than the phenol demanded oxidation potential. Phenol could be oxidized on the valence band of ZnO and TiO₂. Furthermore, merbromin molecules may facilitate the charge transfer between the valence band of semiconductors and the phenol molecules. Merbromin may adsorb the phenol molecules and encourage the charge-transfer process. Thus, the holes generated in the ZnO and TiO₂ valence band, transfer faster toward the phenol molecules through the dye. Hence, the role of the dye molecule in TiO₂ catalytic activity enhancement may be charge-transfer formalism rather than sensitization formalism. In the proposed formalism, the hole transfer from ZnO or TiO₂ valence band to phenol molecules is thermodynamically feasible and the kinetics is enhanced using the dye molecules.

The results are consistent with literature in this aspect [15-16, 24-26].

Phenol degradation rate at the surface of dye-modified ZnO is higher than that of dye-modified TiO₂. The LUMO level of merbromin is calculated to be 910 and 1110 mV more cathodic than the conduction band of TiO₂ and ZnO, respectively. As a result of a large energy gap between the conduction band of ZnO and LUMO of merbromin, a large driving force for electron injection from dye to ZnO conduction band is occurred that could utilize photocatalytic reaction. In addition to the energy potential of the conduction band, in reaction via dye-modified ZnO, the generation of intermediates and their conversion to the products, are done very rapidly so that no perceptible increase in the normalized absorption is shown in the first hour of reaction period (Fig. 8). The fast consumption of the intermediates may be due to more adsorption of these intermediates on the surface of dye-modified ZnO catalyst. Thus, one reason for difference in activities of the catalysts may be due to the difference in adsorption of the intermediates on the surface of these two catalysts. The amount of the merbromin molecules, supported on the surface of photocatalysts, may also influence the photocatalytic activity of the studied semiconductor photocatalysts. A good number of merbromin dye molecules absorbed strongly on the surface of the TiO₂ and blocked the reactive sites on the surface leading to saturation and lower rates of degradation of phenol on the surface of the dye-modified TiO₂ photocatalyst. Furthermore, it is known that aggregation and dimerization reduce the lifetimes of the excited state of dye molecules because of increasing of possibly radiationless excited state dissipation. Therefore, generation of the active oxygen species decreases [3]. Since more dye molecule presence on the surface of TiO₂ nanoparticles in comparison with ZnO, aggregation and dimerization are much probable at the surface of dye-modified TiO₂. So, dye-modified ZnO shows superior efficiency towards phenol removal.

CONCLUSIONS

Results of the present work indicate that the surface adsorbed merbromin dye can modify TiO₂ and ZnO semiconductor for degradation of phenol using visible light. No leaching of merbromin dye was observed during photocatalytic reactions and catalysts were stable throughout

the reaction process. The HOMO position of merbromin is not low enough to oxidize phenol in the visible region. So, the proposed mechanism in the TiO₂ and ZnO impregnated with merbromin systems is charge-transfer formalism instead of sensitization process. Phenol was almost degraded completely in 4 hours on dye-modified ZnO photocatalyst while it was degraded only to 47% on dye-modified TiO₂. Two reasons for difference in reactivity of the catalysts are proposed. The first one could be due to a larger driving force of electron injection from dye to ZnO conduction band because of larger energy gap between the conduction band of ZnO and LUMO of merbromin. The second one is the lower aggregation and dimerization of the dye at the surface of ZnO because of less absorption of dye on ZnO surface. Less aggregation enhances the lifetime of the excited state of the dye molecules and lead to more effective electron injection from LUMO of the dye to the conduction band of ZnO. As a consequence, dye-modified ZnO shows superior photocatalytic performance for phenol degradation compared to the dye-modified TiO₂.

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