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Solar-light induced photodecolorization of water soluble azo-azomethine dye: influence of operational parameters and nanophotocatalysts

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ABSTRACT

Photocatalytic decolorization of a new water soluble azo-azomethine dye, sodium 4-((4-hydroxy-3-((2-(4-(4-(2-hydroxy-5-((4-sulfonatophenyl)diazenyl)benzylide-neamino)butyl) piperazin-1-yl)ethylimino)methyl)phenyl)diazenyl)benzenesulfonate, 2,4-PIP, has been reviewed under solar light and UV irradiation. The effects of experimental parameters such as (i) initial dye concentration, (ii) the nanophotocatalyst dosage, (iii) hydrogen peroxide concentration, (iv) irradiation time, and (v) pH on photodecolorization of the dye have been investigated. The photocatalytic activity of TiO_2 and ZnO on rate and efficiency of decolorization was also investigated. The result indicated that TiO_2 was a valuable alternative nanocatalyst than ZnO for decolorization of the dye in the presence of solar light and UV irradiation at pH 5–7. Furthermore, maximum decolorization of the dye (more than 95%) was occurred in the presence of TiO_2 during 30 min under solar light. The intermediate products of photodecolorization were also identified using gas chromatography–mass spectrometry.

Keywords: Azo-azomethine; Photodecolorization; Solar light; UV irradiation; Nanophotocatalyst

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1. Introduction

Azo dyes are abundant class of colored organic compounds having extensive applications in several industries for producing fabric, furniture, food, electronics, and printing systems [1–3]. Dumping or accidental discharge of dyes wastewater into aquatic systems during dye production and also textile manufacturing process has caused a considerable amount of environmental and health problems, prompting researchers to look for appropriate treatments in order to remove pollutants [4]. During the past decades, conventional methods such as coagulation, microbial degradation, absorption on activated carbon, incineration, biosorption, filtration, sedimentation, chlorination, and ozonization have been used to treat dyes wastewater [5,6]. However, these techniques are non-destructive, since they only transfer the non-biodegradable contaminants into sludge, giving rise to secondary pollution, which requires further treatment or disposal [7–10].

Alternatives to conventional treatment methods for destruction of a broad range of undesirable organic pollutants are advanced oxidation processes (AOPs). AOPs are a set of techniques which normally utilize a strong oxidizing species, mainly $^{\cdot}OH$ radicals to break down macromolecule into smaller and less harmful substances [11,12]. In recent years, AOPs including heterogeneous photocatalytic systems have been shown to be potentially advantageous and useful due to the lack of limitations in mass transfer, the ability

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to be carried out at mild temperature and to completely degrade many organic pollutants [13–15].

A considerable attention has been paid to the semiconductors and quantum dot semiconductors which are irradiated by a light source whose energy is higher than or at least equal to their band gap [16,17]. Among the commonly applied semiconductors, TiO_2 and ZnO with 3.42–3.54 and 3.37 eV band gaps, respectively, have received the greatest interest [18,19]. TiO_2 is found to be the most active photocatalyst under the photon energy of $300\,nm < \lambda < 390\,nm$ [20]. Moreover, good chemical durability and long-term photostability, low toxicity and inexpensive cost of TiO_2 have advanced its wide application in photocatalytic processes [21–23]. On the other hand, low production cost of ZnO and its unique electrical, optoelectronic, and luminescence properties have recently been considered as a promising photocatalyst to degrade and also decolorize azo dyes in industries wastewater under sunlight [24].

Although various reports deal with the photodecolorization of dyestuffs, no study, to the best of our knowledge, has reported on the photocatalytic decolorization of water soluble azo-azomethine dyes. Therefore, the present study manifests the photocatalytic activity of ZnO and TiO_2 nanoparticles for decolorization of a new prepared azo-azomethine dye, sodium 4-((4-hydroxy-3-((2-(4-(4-(2-hydroxy-5-((4-sulfonatophenyl)diazenyl)benzylideneamino)butyl)piperazin-1-yl)ethylimino)methyl)p-henyl)diazenyl)benzenesulfonate, 2,4-PIP, Fig. 1, under both solar light and UV irradiation. In particular, the influence of operational parameters including catalyst dosage, initial concentration of the dye, concentration of H_2O_2, pH, and time of irradiation on decolorization of 2,4-PIP was examined. The performance of ZnO and TiO_2 nanoparticles for decolorization of dye was also compared. The intermediate products of photodecolorization, identified using gas chromatography–mass spectrometry (GC–MS), indicated that cleavage of azo bond was happened and 2,4-PIP was converted to low molecular weight products during irradiation. Furthermore, the effect of ethanol, as a quenchable species, on decolorization of the dye was also investigated.

2. Materials and methods

2.1. Chemicals

All of the chemicals and reagents were of analytical grade and used as received without further purification. ZnO (particle size, ca. <50 nm) and TiO_2 (particle size, ca. 21 nm) nanoparticles were purchased from Aldrich Chemical Co. The azo-azomethine dye, 2,4-PIP, was prepared as described in supplementary materials section.

2.2. Instrumentation

Electronic spectral measurements were carried out using an Optizen 3220 UV spectrophotometer in the range of 200–900 nm. A Metrohm 744 pH meter was used for checking the pH values of the experimental solution. The intermediate reaction products were analyzed by Shimadzu GC–MS-QP 1000 EX. The photocatalytic experiments in the presence of UV irradiation were carried out in a cylindrical batch (10 L) reactor which contains five medium pressure mercury vapor lamps (6 W, Philips TUV G6T5) set in parallel and emitting 365 nm wavelength. It has a reaction chamber with specially designed reflectors made of highly polished stainless steel. Any increase on the temperature due to light irradiation was limited due to the correct dimensioning of the photoreactor and air circulation. Open quartz tube with 24 mL capacity, 20 cm height, and 12 mm diameter was placed vertically in the middle of the photoreactor and used as a reaction vessel, Fig. 2. The experiment in the presence of solar light was carried out using natural sunlight irradiation at 10 am–4 pm during the summer of 2012 in Arak University (Arak, I.R. Iran). The average solar light intensity over the duration of each experiment was measured using LT Lutron LX-10/A Digital Lux meter and the intensity was 1,300 ± 100 lux.

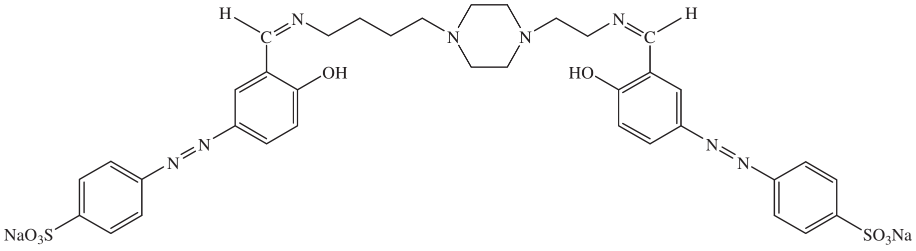

Fig. 1. Chemical structure of 2,4-PIP.

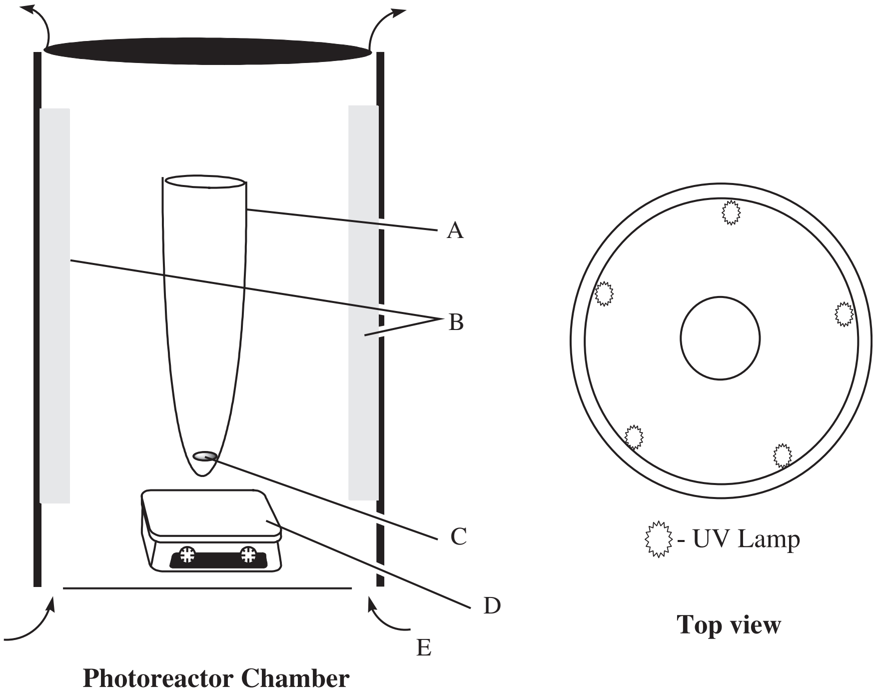

Fig. 2. Scheme of the photoreactor used for photocatalytic experiment, A: quartz batch reactor, B: UV lamp assembly, C: magnetic stirrer, D: stirrer, E: air flow.

2.3. Photodecolorization studies

Experiment for standardization of H_2O_2 concentration was conducted during 30 min. The reaction solution containing the dye (33 ppm) at natural pH in double-distilled water (10 mL) was stirred under solar light. The reaction was initiated by adding different amounts of hydrogen peroxide to the solution (0.1–2.5 g/L). After 30 min, samples were periodically taken out and the absorbance of the band at about 345 nm was recorded. Also, the photocatalytic experiments were carried out in a photoreactor with the following process.

Initially, nanoparticles were suspended into 10 mL deionized double-distilled water. The respective mixtures were kept in ambient temperature and homogenized by shaking for 30 min to make constant concentration. Then 2 mL of the solution was added into quartz tube containing the dye and H_2O_2 in double-distilled water (10 mL) in dark. The pH values of the solutions were adjusted at desired level using dilute NaOH and HCl (the natural pH of the reaction solution was 5–5.5). Finally, the quartz tube containing the dye, H_2O_2, and photocatalyst was transferred to photoreactor and/or direct sunlight. At regular time intervals, 2 mL of the sample was withdrawn and centrifuged to separate the catalyst. Then the UV–vis absorption spectrum of the clarified solution at 200–900 nm was recorded. The absorbance of the band at about 345 nm was used to monitor decolorization of the dye. A parallel blank test without photocatalyst and oxidant was carried out in each time. Photocatalytic decolorization percentage of the dye was determined using the following equation, Eq. (1):

$$\text{Decolorization efficiency } (\%) = \frac{C_0 - C_f}{C_0} \times 100 \qquad (1)$$

where C_0 is the initial concentration of the dye and C_f is the concentration of the dye after photoirradiation.

3. Results and discussion

3.1. UV–vis spectra changes

The UV–vis spectrum of 2,4-PIP exhibit absorption band with a maximum at 345 nm attributed to the $\pi \rightarrow \pi^*$ transition involving the π-electrons of azo and azomethine groups. Time-dependent UV–vis spectrum of 2,4-PIP during photoirradation processes in the presence of TiO_2, at initial pH, is shown in Fig. 3. Decolorization percent was recorded with respect to the change in the intensity of main absorption band which decreased and finally disappeared. No new absorption bands appeared in either the visible or ultraviolet regions and complete decolorization of the dye occurred after 30 min in optimized condition.

3.2. Effect of H_2O_2 concentration

In order to investigate the effect of H_2O_2 dosage on decolorization efficiency of the dye, experiments were conducted at varied concentrations of oxidant between 0.1 and 2.5 g/L under solar light. The concentration of 2,4-PIP was kept constant (33 ppm) at pH 5.5 and the irradiation time of 30 min was selected (see supplementary materials). The results revealed that the decolorization efficiency increased with increasing of H_2O_2 concentration up to 0.5 g/L. So, with increasing of hydrogen peroxide concentration, the formation of hydroxyl radicals was enhanced, Eq. (2) [25,26].

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \tag{2}$$

However, with further increasing H_2O_2 concentration, decolorization efficiency of the dye was decreased. This is due to scavenging nature of hydrogen peroxide towards $^{\bullet}OH$ radicals and formation of perhydroxyl radicals which are significantly less reactive than hydroxyl radicals, Eq. (3) [25,27].

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{3}$$

3.3. Effect of photocatalyst nanoparticles

Experiments were carried out in the presence of optimal dosage of hydrogen peroxide, 0.5 g/L, and TiO_2 and/or ZnO photocatalysts at initial pH and fixed concentration of the dye (33 ppm). As it is shown in Fig. 4, when experiments were performed with TiO_2 and ZnO under solar light, 100 and 70.4% of the dye were decolorized after 30 min, respectively. However, in the absence of nanocatalysts, no decolorization was achieved in the same duration.

Similar trend was observed for decolorization of the dye under UV irradiation.

$$\text{Photocatalyst} + h\nu \rightarrow e^{-}_{CB} + h^{+}_{VB} \tag{4}$$

$$h^{+}_{VB} + \text{dye} \rightarrow \text{dye}^{\bullet +} \rightarrow \text{Oxidation of the dye} \tag{5}$$

When experiments were performed in the presence of TiO_2 and under UV irradiation, 100% decolorization of 2,4-PIP occurred after 120 min, while in the presence of ZnO 80.1% decolorization was achieved in the same duration. Fig. 5 depicts the photodecolorization efficiency of two mentioned nanocatalysts comparatively, as a function of time under UV irradiation. Surface area, particle size, and dye adsorption capacity of TiO_2 play key roles in enhancing decolorization efficiency of TiO_2 than ZnO under both solar light and UV irradiation [4,28].

3.4. Effect of photocatalyst loading

According to our best knowledge from the literatures [21,29,30], the rate and also efficiency of dye decolorization is affected considerably by the amount of TiO_2 and ZnO nanoparticles. In order to optimize the dosage of photocatalysts, the decolorization of 2,4-PIP was carried out by varying TiO_2 and ZnO concentration from 0.33 to 2.3 g/L. The result obviously revealed that the photodecolorization efficiency was enhanced by increasing photocatalyst concentration up to 0.66 and 1.6 g/L for TiO_2 and ZnO, respectively.

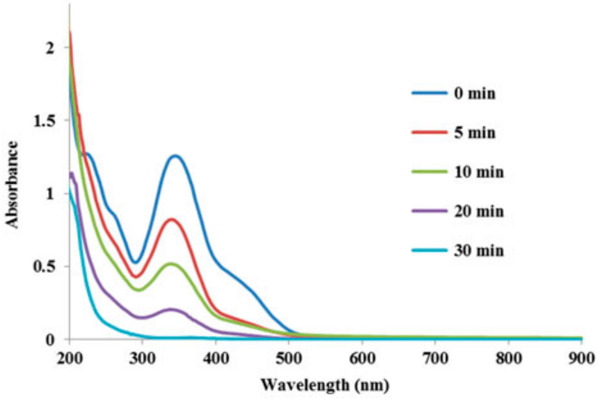

Fig. 3. Time-dependent UV–vis absorption spectra of 2,4-PIP (33 ppm) under solar light in the presence of TiO_2 (0.66 g/L) and H_2O_2 (0.5 g/L) during 30 min, pH 5.5.

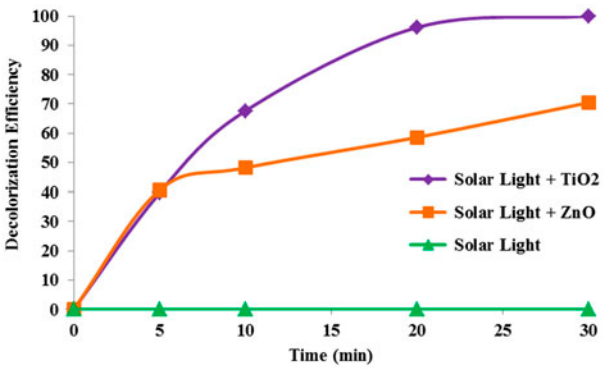

Fig. 4. Photocatalytic decolorization of 2,4-PIP (33 ppm) under direct sunlight in the presence of TiO_2 (0.66 g/L) and ZnO (1.6 g/L) at pH 5.5.

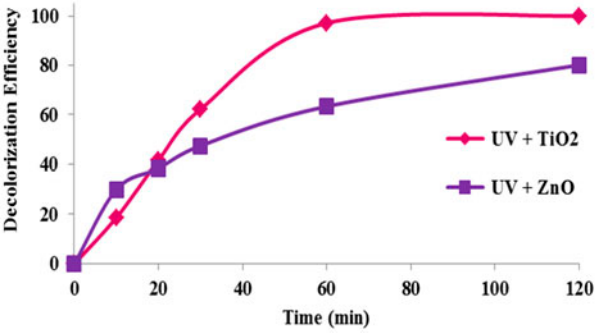

Fig. 5. Photocatalytic decolorization of 2,4-PIP (33 ppm) under UV irradiation in the presence of TiO_2 (0.66 g/L) and ZnO (1.6 g/L) at pH 5.5.

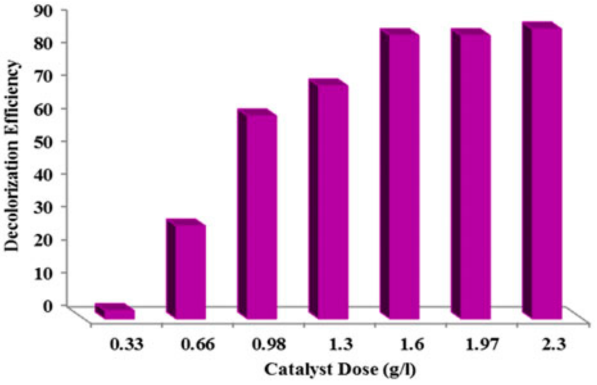

Fig. 6. Effect of ZnO dosage on photocatalytic decolorization of 2,4-PIP (33 ppm) during 30 min. H_2O_2 (0.5 g/L), pH 5.5.

Indeed, the number of active sites on the nanophotocatalyst surface increases with the increasing of catalyst dosage. Thus, the number of ·OH radicals which can take part in actual decolorization of the dye is also increased [21]. However, at high concentration of photocatalyst, the photodecolorization efficiency of the dye was decreased or remained constant. This result was thought to be in terms of increasing in turbidity of the suspension with high dosage of photocatalyst [21]. Consequently, increasing photocatalyst concentration impedes light penetration and hence photoactivated volume of suspension was reduced [29,30]. Fig. 6 shows the effect of ZnO amount on photocatalytic decolorization of 2,4-PIP under solar light at initial pH during 30 min (for TiO_2 see supplementary materials).

The further studies were performed in the optimum concentration of photocatalysts.

3.5. Effect of initial dye concentration

The effect of initial dye concentration on decolorization process was evaluated by varying the dye concentration from 26 to 57 ppm under optimized concentration of photocatalysts. From Fig. 7, it is evident that the decolorization efficiency of 2,4-PIP decreased while the initial dye concentration was increased. Actually, the solution becomes more intensely colored as the dye concentration was increased. Furthermore, at this condition, the concentration of adsorbed dye on the surface of photocatalyst was increased. Therefore, the path length of photons entering the solution decreases and fewer of photons reach to the catalyst surface. With inhibition of hydroxyl radicals production, the decolorization efficiency of the dye was also significantly reduced [31].

3.6. Effect of time on decolorization of the dye under solar light and UV irradiation

Fig. 8(a) illustrates the decolorization efficiency of 2,4-PIP under direct sunlight and UV irradiation in the presence of optimum concentration of hydrogen peroxide and in the absence of photocatalysts. It is evident that the decolorization efficiency of the dye was increased with increasing of irradiation time. Also, in the absence of photocatalysts decolorization of the dye during 30 min was negligible

In the presence of optimum concentration of TiO_2, 100 and 62.2% decolorization occurred during 30 min under direct sunlight and UV irradiation, respectively (Fig. 8(b)).

It should be also mentioned that similar trend was observed for ZnO. As shown in Fig. 8(c), in the presence of ZnO 70.4 and 47.4% decolorization was achieved during 30 min under direct sunlight and UV irradiation, respectively. Our results are in agreement with the earlier findings [29,32].

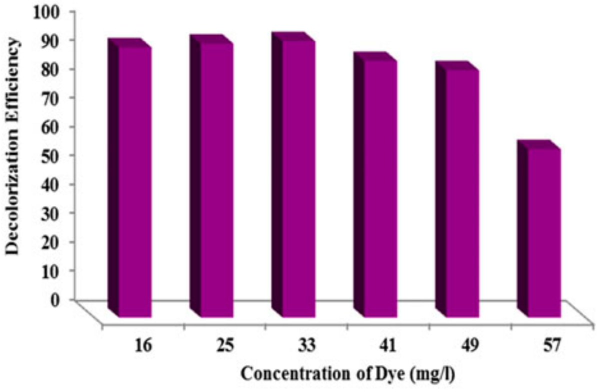

Fig. 7. Effect of initial dye concentration on solar light decolorization of 2,4-PIP in the presence of TiO_2 (0.66 g/L) and H_2O_2 (0.5 g/L) during 30 min at pH 5.5.

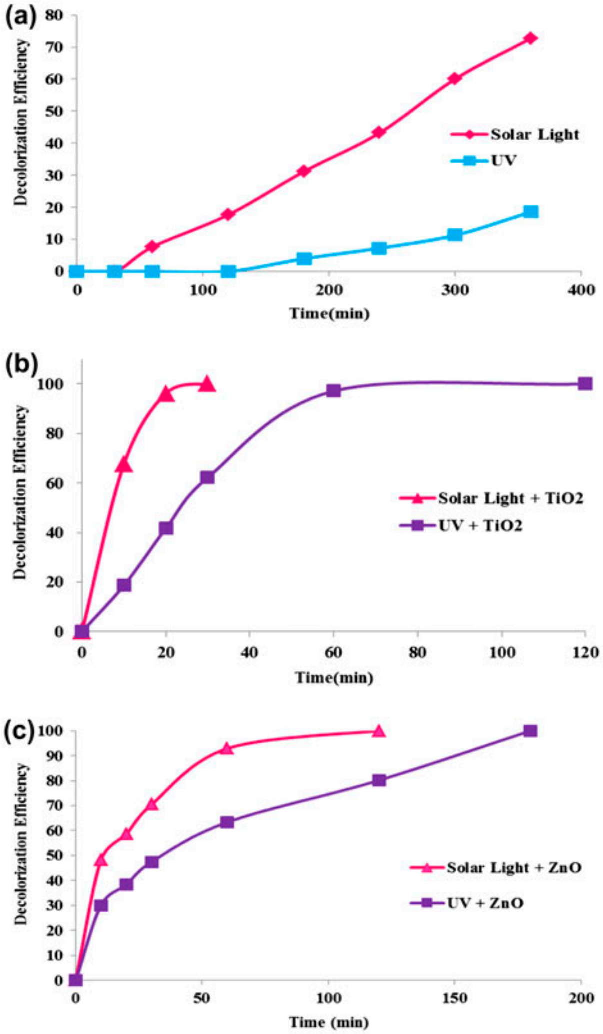

Fig. 8. Comparison of solar/UV irradiation on decolorization of 2,4-PIP (33 ppm) at pH 5.5 in the presence of (a) H_2O_2 (0.5 g/L); (b) TiO_2 (0.66 g/L), H_2O_2 (0.5 g/L); (c) ZnO (1.6 g/L), H_2O_2 (0.5 g/L).

3.7. Effect of pH

The formation of hydroxyl radicals, as a non-selective oxidizing agent, during decolorization process of wastewaters is based on solution pH [21,33,34]. However, the interpretation of pH effects on efficiency of dye photodecolorization process, because of its multiple roles, is very difficult task. Firstly, pH changes can influence on the adsorption of the dye molecules onto nanoparticles surfaces, an important step for the photocatalytic oxidation to take place. For example, the TiO_2 surface is positively charged in acidic media ($pH < 6.8$), whereas it is negatively charged under alkaline conditions ($pH > 6.8$) [9]. Secondly, hydroxyl radicals are considered as the predominant species at neutral or high pH levels [35]. It was stated that in alkaline solution $^{\cdot}OH$ are easier to be generated by oxidizing more hydroxide ions available on nanoparticle surface [35].

$$h^+_{VB} + OH^- \rightarrow HO^{\cdot} \tag{6}$$

Thirdly, the nanoparticles tend to agglomerate under extreme acidic condition and the available surface area for dye adsorption and also photon absorption would be reduced [35]. Hence, pH plays an important role in both the characteristics of wastewaters and in the reaction mechanisms that can contribute to the dye decolorization, namely, hydroxyl radical attack, direct oxidation by the positive hole, and/or direct reduction by the electron in the conducting band.

In order to study the effect of pH on the dye decolorization efficiency, experiments were carried out at various pH values, ranging from 2 to 10 for constant concentration of the dye (33 ppm) and nanocatalysts loading (0.66 and 1.6 g/L, respectively, for TiO_2 and ZnO). Fig. 9 indicates the decolorization efficiency of 2,4-PIP during 30 min direct sunlight irradiation as function of pH. It has been observed that in the presence of TiO_2, the lesser decolorization of 2,4-PIP occurred in pH 10. Whereas, in the presence of ZnO, the lesser decolorization occurred at both extreme acidic and alkaline range (pH 2 and 10). The influence of pH on decolorization efficiency of 2,4-PIP in the presence of TiO_2 can be explained on the basis of acid–base property of nanocatalyst surface. The point of zero charge (PZC) of TiO_2 is at pH 6.8 [35]. Thus, the TiO_2 surface is positively charged in acidic media ($pH < 6.8$), whereas it is negatively charged under alkaline conditions ($pH > 6.8$) [9].

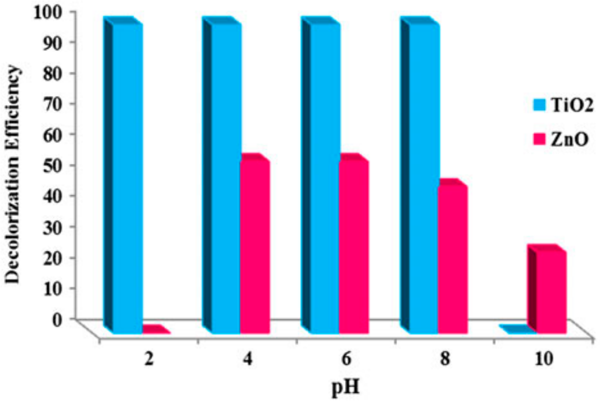

Fig. 9. Effect of pH on decolorization efficiency of 2,4-PIP (33 ppm) under direct sunlight during 30 min. TiO_2 (0.66 g/L) and ZnO (1.6 g/L).

$$\mathrm{TiOH} + \mathrm{H}^+ \rightarrow \mathrm{TiOH_2}^+ \quad (7)$$

$$\mathrm{TiOH} + \mathrm{OH}^- \rightarrow \mathrm{TiO}^- + \mathrm{H_2O} \quad (8)$$

Thus, enhancement of decolorization efficiency of the dye in acidic condition can be ascribed on the basis of electrostatic interactions between the positive TiO_2 surface and the dye anions [36]. In addition, 2,4-PIP has sulfuric groups in its structure, which is negatively charged in alkaline conditions. Hence, in the alkaline solution, the dye may not be adsorbed onto photocatalyst surface, Eq. (8) [29].

On the other hand, the PZC of ZnO is at pH 9.0 ± 0.3 [29]. Thus, the ZnO surface is positively charged below pH 9 whereas is negatively charged above pH 9. In slightly acidic or neutral solution, photodecolorization efficiency of the dye was more than that in extreme acidic and alkaline solutions, Fig. 9. The lower decolorization efficiency of the dye in the presence of ZnO at pH 2 can be explained on the basis of ZnO photocorrosion in extreme acidic solution [33,34]. The photocorrosion of ZnO is complete at pH lower than 4, as reported previously [34].

At pH 4 and higher than 4, no photocorrosion of ZnO occurs. Although, more efficient formation of hydroxyl radicals occurs in alkaline solution under illumination, Eq. (6), 2,4-PIP has sulfuric groups in its structure which is negatively charged in alkaline conditions. Thus, in alkaline solution, the dye may not be adsorbed onto photocatalyst surface effectively [29].

3.8. Effect of ethanol

As previously reported, in the presence of alcohols, such as ethanol, a significant retardation effect on decolorization efficiency of the dyes was achieved [26,33]. This is due to the ability of alcohols to quench of hydroxyl radicals [33]. It was observed that small amounts of ethanol inhibited decolorization of 2,4-PIP which means that hydroxyl radicals play a major role in photocatalytic decolorization process. For example in the presence of 10% (v/v) ethanol in optimized conditions, the photodecolorization efficiency decreases from 96 to 64% after 20 min under direct sunlight (see supplementary materials).

3.9. Adsorption of 2,4-PIP on the surface of photocatalyst

In order to investigate the possible adsorption behavior of 2,4-PIP at different pH values, the suspensions were prepared by mixing 10 mL of dye solutions (33 ppm) with fixed catalyst dose for 60 min. The suspensions were kept in the dark under stirring condition and filtered and being centrifuged. The results are reported in supplementary materials. From the results, we noticed that maximum adsorption of dye happens in slightly acidic pH (about 15.74% at optimum pH value 6). While in basic media, the surface is less positively charged leading to lower adsorption of anionic dye [37].

3.10. GC–MS analysis

To identify the reaction intermediates, GC–MS experiment was conducted. For this aim, the samples were prepared by extraction of part (20 mL) of irradiated solution (after removal of nanoparticles) with dichloromethane (5×20 mL). The extracts were dried on anhydrous Na_2SO_4 overnight. The collected organic solution was allowed to be concentrated under reduced pressure to 1 mL and then analyzed by GC–MS. The GC–MS spectra and chemical structure of analyzed compounds along with retention time and molecular weight are depicted in supplementary materials.

According to GC–MS analysis and results reported by other workers [2,38], we propose that decolorization process is initialized by cleavage of the azo bond to form several fragments with lower molecular weight. Then, the electrophilic attack of $^{\cdot}OH$ radical on aromatic ring leads to yield hydroxylated derivatives. Simultaneously, the imino groups undergo cleavage followed by saturation with $^{\cdot}H$ radicals generated during reaction. Ultimately, the successive attack of $^{\cdot}H$ radicals concomitant oxidative ring opening forms acids such as adipic acid, malonic acid, propanoic acids, and other organic acids which can be converted to CO_2 and H_2O [2].

4. Conclusion

Photodecolorization of a new water soluble azo-azomethine dye, 2,4-PIP, has been studied under solar light and UV irradiation assisted with TiO_2 and ZnO nanoparticles. The results indicated that the degree of decolorization was obviously affected by important operating parameters such as irradiation time, catalyst loading, pH of solution, initial dye concentration, and also hydrogen peroxide concentration. On the basis of our work, optimum H_2O_2 concentration for decolorization of the dye was 0.5 g/L. The photodecolorization efficiency increased with increase in catalyst dosage up to an optimum loading (0.66 g/L for TiO_2 and 1.6 g/L for ZnO). The result also revealed that photodecolorization efficiency was decreased as initial concentration of the dye was increased. Moreover, it has been observed that the lesser decolorization of the dye in the presence of TiO_2 occurred at pH 10. While, in the case of ZnO, the lesser decolorization of the dye was achieved at pH 2. Further study showed that the addition of small amount of ethanol can inhibit the photodecolorization of the dye. From the inhibitive effect of ethanol, it was detected that hydroxyl radicals played a significant role in decolorization of the dye. It was also found that the photocatalytic decolorization occurred at a faster rate under direct sunlight compared to that of UV irradiation (365 nm). The performance of photocatalytic activity has clearly exhibited that TiO_2 is the more efficient photocatalyst for decolorization of the dye than ZnO under both direct sunlight and UV irradiation.

Acknowledgment

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Electronic supplementary material

The procedure for preparation of 2,4-PIP, effect of pH, H_2O_2, and TiO_2 dosage on decolorization of the dye, GC–MS spectra along with chemical structures of intermediate products can be obtained free of charge via http://www.araku.ac.ir/~h_khanmohammadi/Supportinginformation-12.pdf.

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