

Photodegradation of Congo Red in Aqueous Solution on ZnO as an Alternative Catalyst to TiO₂

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(Received 14 November 2007, Accepted 24 August 2008)

In this research, the efficiency of ZnO and TiO₂ was compared by photocatalytic degradation of Congo red azo dye. The effects of some parameters such as pH, dye concentration and irradiation time on the degradation rate of dye solution were also examined. In addition, the aggregation feature of Congo red was studied by using UV-Vis spectroscopy techniques. The recovery of the ZnO catalyst was also investigated.

Keywords: Photocatalytic degradation, Aggregation, Congo red, Zinc oxide

INTRODUCTION

Azo dyes are a versatile class of colored organic compounds that have extensively been used in industry for applications such as textiles, paper, leathers, additives and analytical chemistry [1]. During dye production and textile manufacturing processes, a large quantity of waste water containing dyestuffs with intensive color and toxicity are introduced into the aquatic systems [2]. In such cases, removing color from wastes is imperative, because the presence of even small amounts of dyes (below 1 ppm) is clearly visible and influences water environment considerably.

The degradation of azo dyes has been reported in many papers [3-7]. It is necessary to find an effective method of wastewater treatment in order to remove color from effluents. Physical and chemical techniques such as coagulation, adsorption on activated carbon, ultra filtration and reverse osmosis are generally used efficiently to remove dyes from textile wastewater. However, these processes are considered as nondestructive since they merely transfer the dye from liquid

to solid wastes. Consequently, the regeneration of the adsorbent material and post-treatment of solid wastes, which are expensive operations, are needed [8,9].

Advanced oxidation processes (AOPs) are alternative techniques of destruction of dyes and many other organics in wastewater and effluents. These processes generally involve UV/H₂O₂, UV/O₃ or UV/Fenton's reagent for the oxidative degradation of contaminants [10]. Among the various AOPs, semiconductor-mediated photocatalysis has been given great credit over the past few years due to its potential to destroy a wide range of organic and inorganic pollutants at ambient temperatures and pressures, with no harmful by-products [11]. The most commonly studied catalysts are TiO₂, ZnO, Fe₂O₃, ZnS, WO₃ and CdS. In order to achieve a more effective photocatalytic degradation, it is necessary to consider the surface charge property of semiconductors and nature of dye molecules. pH affects the surface charge of semiconductors and can also lead to aggregation phenomenon in dye solutions. Aggregation is one of the features of dyes in solution and ionic dyes tend to aggregate in diluted solutions, leading to dimmer formation and sometimes even higher order aggregates [12,13].

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In this work, the effects of some parameters such as aggregation feature of Congo red, dye concentration, pH, irradiation time and types of catalysts on the degradation rate of dye solution were examined. Moreover, the recovery of the ZnO catalyst was investigated.

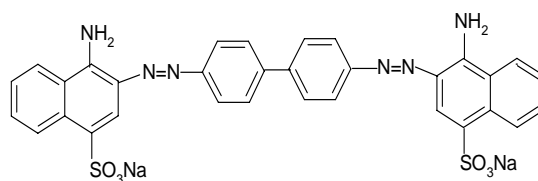
EXPERIMENTAL

Materials and Instrumentation

Congo red (C.I. Direct Red 28, M.W. = 696.67 g mol⁻¹ C₃₂H₂₄N₆O₆S₂.2Na), sodium hydroxide, hydrochloric acid, titanium dioxide powder (anatase, particle size: 30 nm) and ZnO powder (particle size: 200 nm) were obtained from Merck. Solutions were prepared by dissolving appropriate amount of the dye in double distilled water before each experiment. The dye chemical structure is shown in Scheme 1.

Photocatalytic experiments were performed in open Pyrex vessel of 50 ml capacity. The radiation source, a UV lamp (30 W, UV-C, $\lambda = 253.7$ nm, photon providing 4.89 eV, manufactured by Philips, Holland), was irradiated perpendicularly to the surface of solution, and the distance between the UV source and vessel containing reaction mixture was fixed at 15 cm. Air was blown into the reaction by an air pump to maintain the solution saturated with oxygen during the course of the reaction. The experiments were performed at ambient temperature at 32 °C. The suspension pH values were adjusted at desired level using 0.01 N NaOH or 0.01 N HCl solutions and, then, the pH values were measured *via* pH meter (Metrohm744). For all the experiments, Photocatalyst amount was 0.5 g l⁻¹. Before irradiation, dye solution was stirred in the dark for 10 min after the addition of the catalyst. Next, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous. The suspension was sampled at regular intervals and immediately centrifuged at 3500 rpm for 10 min to completely remove catalyst particles.

The progress of photocatalytic degradation was monitored by Chemical Oxygen Demand (COD) analysis which was measured by the dichromate reflux method [14]. The concentration of the solution samples was measured by UV-Vis spectrophotometer (Shimadzu UV 2100). Making use of the latter method, conversion percentage of Congo red was obtained at different intervals. Absorption peaks



Scheme 1. Structure of Congo red (C.I. Direct Red 28)

corresponding to Congo red appeared at 497, 347 and 237 nm. The degree of photodegradation (X), as a function of time, was calculated by $X = (C_0 - C)/C_0$ where C_0 is the initial concentration of dye, and C the concentration of dye at time t.

RESULTS AND DISCUSSION

The Effect of UV Irradiation and ZnO Particles

Control experiments were carried out since some dyes are degraded by direct UV irradiation [15]. One set was performed with Congo red solution exposed to ZnO without the presence of UV light (the ZnO adsorption). The second set was done by exposing Congo red solution to UV without the presence of ZnO (the photolysis condition). The third set was performed through exposing Congo red solution to UV irradiation in the presence of ZnO (the photocatalysis condition). The results are presented in Fig. 1.

These experiments demonstrated that both UV light and photocatalyst are needed for the effective destruction of Congo red. The mechanism of ZnO-photocatalyzed reactions has

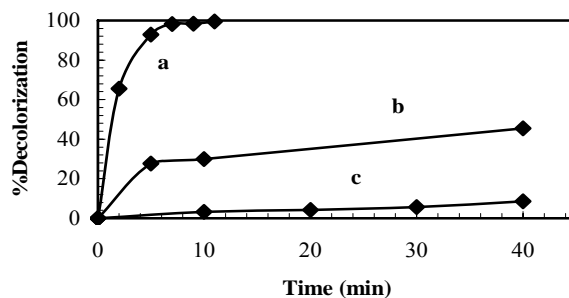
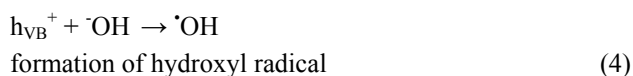
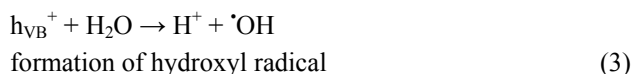
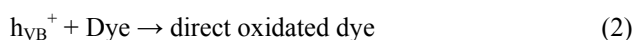
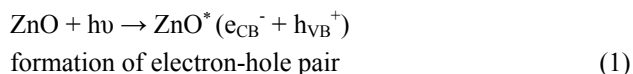


Fig. 1. Effect of UV light and ZnO on photocatalytic degradation of Congo red (5 ppm), ZnO = 0.5 g l⁻¹: (a) ZnO + UV + air bubbling, (b) ZnO + air bubbling and (c) UV + air bubbling.

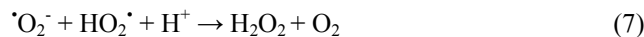
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been a subject of extensive research [16]. Although the detailed mechanism differs from one pollutant to another, it has been widely recognized that hydroxyl radical $\cdot\text{OH}$ acts as active reagent for the mineralization of organic compounds.

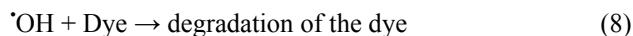
The radicals are formed by the scavenging of their electron-hole pair by molecular oxygen and water (Eqs. 1-4).



Electrons in the conduction band (e_{CB}^-) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. 5). This radical, in the presence of organic scavengers, may form organic peroxides (Eq. 6) or hydrogen peroxide (Eq. 7).



Electrons in the conduction band are also responsible for the production of hydroxyl radicals which have been shown to be the primary cause of organic matter mineralization (Eq. 8).



The photo corrosion of ZnO is complete at pH lower than 4 [17,18] and ZnO can be photo-oxidized to Zn(II) and oxygen (Eqs. 9 and 10). Therefore, comparative experiments were performed at pH values higher than 4.

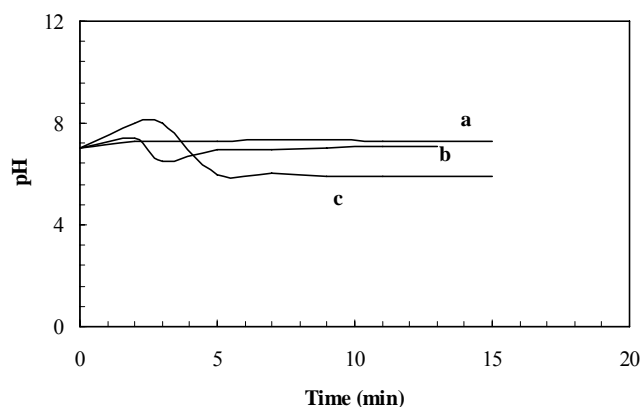
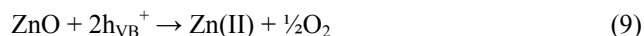


Fig. 2. pH changes of the solution during photooxidation of Congo red with irradiation time, conditions: $C_0 = 5$ ppm, amount of catalyst (0.5 g l^{-1}): (a) ZnO + air, (b) ZnO + UV and (c) ZnO + UV + air.

Figure 2 shows pH changes of the solution during photooxidation of Congo red under different conditions.

UV-Vis Spectral Changes of the Solution as a Function of Irradiation Time

Figure 3 shows typical UV-Vis spectra obtained during the ZnO-mediated photocatalytic degradation of aqueous solution of Congo red under (UV-C) irradiation.

After adding ZnO particles and upon reaching equilibrium in dark for 10 min, the absorbance decrease reflects the adsorption extent of the dye on the ZnO surface. Congo red is strongly adsorbed on ZnO particles surfaces through the two oxygen atoms of the sulfonate group of the dye molecules. The decrease of the absorbance was calculated to be about 20% under the conditions employed. UV light illumination of the aqueous Congo red ZnO suspension causes the absorption bands of the dye in the visible region to decrease as time passes and, finally, to disappear, indicating the destruction of its chromophoric structure in the vicinity of the azo-linkage. This is accompanied by a parallel decrease of the intensities of the bands in the ultraviolet region located at 235 and 347 nm, attributed to the benzoic and naphthalene rings, respectively. No new absorption bands appeared in either the visible or the ultraviolet spectra regions. Figure 4 shows normalized absorbance at 497, 235 and 347 nm which are plotted as functions of irradiation time.

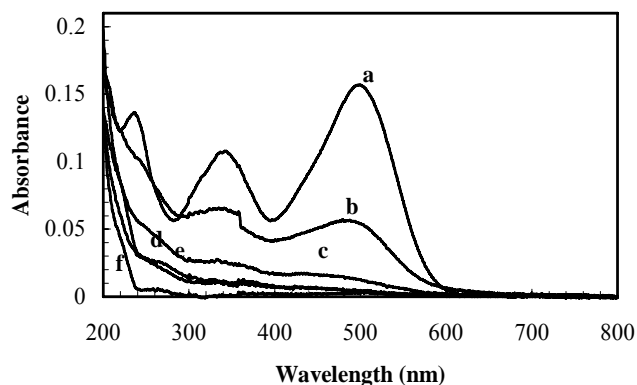


Fig. 3. UV-Vis spectra changes of Congo red (5 ppm) in aqueous ZnO dispersion (0.5 g l⁻¹) irradiated with a mercury lamp light 30 W (UV-C) at varying times: 0 (a), 2 (b), 5 (c), 7 (d), 9 (e) and 11 min (f).

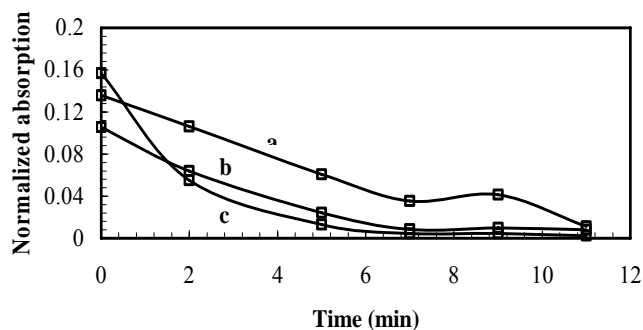


Fig. 4. Normalized absorbance at 497, 235 and 347 nm Congo red (5 ppm) in aqueous ZnO suspension (0.5 g l⁻¹) at different wavelengths: 235 nm (a), 347 nm (b) and 497 nm (c).

It was observed that the intensity of the visible light chromophore band of Congo red (azo-linkage) decreased as a function of time and disappeared after 11 min, resulting in complete decolorization and a 30% of mineralization of the solution, based on UV-Vis spectra and COD value. COD values have been related to the total concentration of organics in the solution and their decrease reflects the degree of mineralization. The reusability of the photocatalyst was tested. The recovered catalyst was reused for four consecutive runs. Figure 5 shows only a slight decrease in the activity of ZnO photocatalyst after four consecutive uses. After reaction was

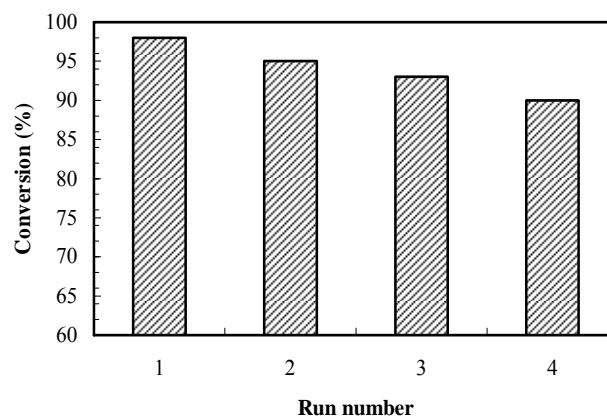


Fig. 5. Effect of ZnO reuse on photocatalytic decolorization after 11 min irradiation.

run, the photocatalyst was analysed by XRD and IR. The nature of the catalyst did not change before or after the experiment.

In general, Azo dyes such as Congo red with N=N azo group also yield gaseous dinitrogen under photocatalytic conditions, which is the ideal condition for the elimination of nitrogen containing pollutants. The aromatic rings were submitted to successive attacks by photogenerated $\cdot\text{OH}$ radicals leading to hydroxylated metabolites before the ring opening and the final evolution of CO_2 induced by repeated subsequent “photo-kolbe” reactions with carboxylic intermediates. According to literature, sulfur heteroatoms are converted into innocuous SO_4^{2-} ions [19]. Figure 6 shows comparison of the activities of titanium dioxide and zinc oxide at $\lambda = 497$ nm.

It was observed that zinc oxide was a very promising photocatalyst for decolorization of Congo red azo dye.

The Effect of the Initial Dye Concentration

The influence of initial concentration of the dye solution on the photocatalytic degradation is a significant aspect of the study. The initial concentrations of Congo red were selected in the range of 5-30 ppm and it was revealed that the percentage of photodegradation decreased as initial concentration of the dye solution increased, as shown in Fig. 7.

One possible explanation of such circumstances is that as initial concentration increases, more and more organic

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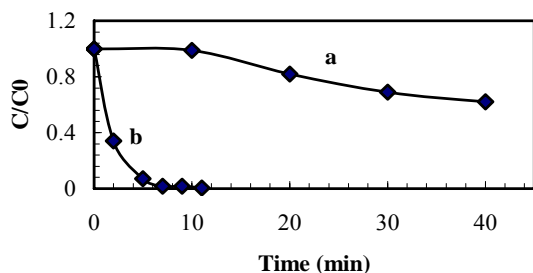


Fig. 6. Comparison of the activities of titanium dioxide (a) and zinc oxide (b) at $\lambda = 497$ nm.

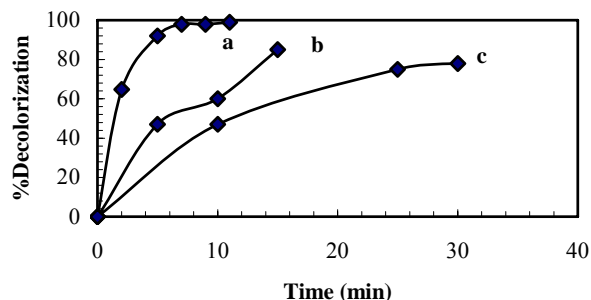


Fig. 7. Effect of the initial dye concentration on photocatalytic degradation of Congo red: (a) 5.7 ppm, (b) 14 ppm, (c) 28 ppm.

substances are adsorbed on the surface of ZnO; therefore, the generation of hydroxyl radicals is reduced, since there are only fewer active sites in the system causing little adsorption of hydroxyl ions, which in turn leads to the decrease in the generation of hydroxyl radicals. Further, as the concentration of a dye solution increases, the photons get intercepted before they could reach the catalyst surface, hence the absorption of photons by the catalyst decreases, and consequently, the degradation percentage is reduced [20]. As it is illustrated in Fig. 7, more irradiation time was required as dye concentration increased.

Kinetics of Photocatalytic Degradation of Congo Red

The initial concentration influence of compounds in the photocatalytic degradation rate of most organic compounds is also described by pseudo-first-order kinetics. Photodegradation rates of chemical compounds on semiconductor surfaces follow the Langmuir-Hinshel

Wood model [19,21].

$$R = dC/dt = k_r \theta = k_r KC / (1 + KC) \quad (11)$$

where k_r is the reaction rate constant, K is the adsorption coefficient of the reaction, and C is the reactant concentration. The values of k_r and K are used to explain the coefficients defining the rate determining reaction events, and pre-equilibrium adsorption within an adsorbed monolayer at the oxide surface and the aqueous solution interface, respectively. The effect of light intensity is also incorporated in k_r , and K especially expresses the equilibrium constant for fast adsorption-desorption processes between surface monolayer and bulk solution [22]. Integration of (Eq. 11) yields the following (Eq. 12):

$$\ln(C_0/C) + K'(C_0 - C) = k_r Kt \quad (12)$$

When the initial concentration C_0 is small, (Eq. 12) changes into (Eq. 13), which expresses a pseudo-first order reaction kinetic regime.

$$\ln(C_0/C) = k_r Kt = kt \quad (13)$$

which yields half life $t_{1/2}$ (in min) that is $t_{1/2} = 0.693/k$, where k is the pseudo-first-order reaction rate constant, $k = k_r K$ in min^{-1} . A plot of $\ln(C_0/C)$ versus t for different concentrations of dye is shown in Fig. 8.

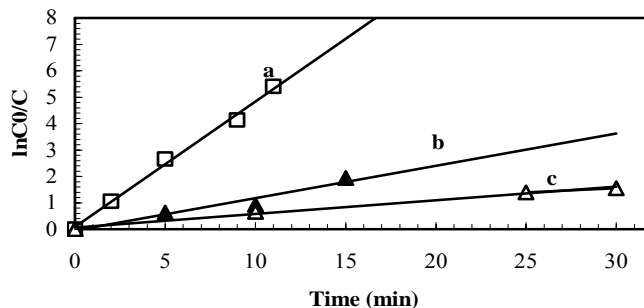


Fig. 8. Plot of photodegradation rate of Congo red on ZnO aqueous solution vs. irradiation time at different dye concentrations: (a) 5.7, (b) 14 and (c) 28 ppm.

In order to study the nature of the photochemical reaction with ZnO, apparent rate constant (k) is calculated from the slopes of the plots for Congo red (see Table 1). The k values depend on the initial concentration of the compounds, which decreases gradually along with the increase in the initial concentration of the compounds.

The Effect of pH Values

The effect of pH on the rate of photocatalytic degradation was studied by keeping all the other experimental conditions constant and changing the initial pH values of Congo red from 6 to 11, the results of which are illustrated in Fig. 9.

Figure 10 shows normalized absorbance at 497, 347 and 235 nm which is plotted as a function of irradiation time at pH = 8.

It was observed that the intensity of the visible light chromophore band of Congo red, $\lambda = 497$ nm, decreased as time passed and disappeared after 8 min of irradiation. It was observed that decolorization of the dye solution was completed but mineralization was not.

Figure 11 shows the absorption spectra of Congo red (5 ppm) in aqueous solution at different pH's.

The results showed an aggregate feature in acidic aqueous solutions with a red shift compared to monomer in the UV-Vis absorption spectra which is due to dimmer molecules. Furthermore, freshly prepared aqueous Congo red dye solution in pH's including neutral and basic did not influence the UV-Vis absorption spectra which means that the aggregation did not occur. Experiments showed that Congo red molecules possessed aggregation in acidic aqueous solution at longer times. By decreasing the solution pH, dye molecule aggregation occurred at shorter time. According to Fig. 12, both monomer and dimmer molecules exist in highly acidic solutions (pH = 0.25).

The efficiency of photocatalytic processes strongly depends upon the pH of the reaction solution. Because of the amphoteric behavior of most semiconductor oxides, an important parameter governing the rate of reaction takes place on semiconductor surface. Normally, the different behavior of each semiconductor in relation to pH can be explained by unlike modifications of the surface properties, mainly due to the isoelectrical point (pH 6.0 for TiO₂ and 9.0 for ZnO) [23,24]. Thus, the semiconductor surface is positively or

Table 1. Effect of Congo Red Concentration. [ZnO] = 0.5 g l⁻¹

| Initial concentration (ppm) | k (min ⁻¹) | $t_{1/2}$ (min) |
|-----------------------------|--------------------------|-----------------|
| 5.7 | 0.4747 | 1.45 |
| 14 | 0.1222 | 5.67 |
| 28 | 0.0517 | 13.40 |

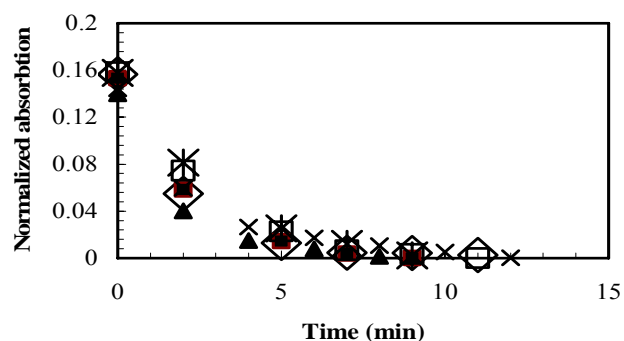


Fig. 9. Comparison of the activities of ZnO (0.5 g l⁻¹) at $\lambda = 497$ nm and different pH: (- - -) 6, (*) 7, (Δ) 8, (\diamond) 9, (\square) 10 and (\blacklozenge) 11.

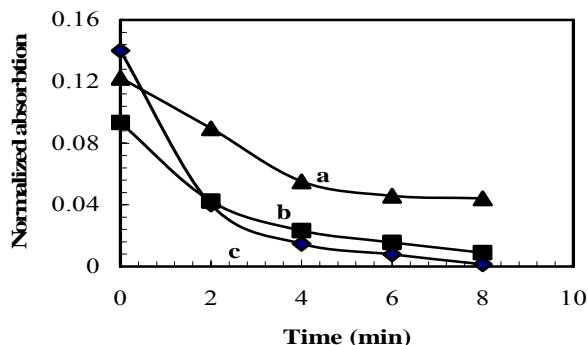


Fig. 10. Normalized absorbance of main UV-Vis bands of Congo red (5 ppm) in aqueous ZnO suspension (0.5 g l⁻¹) at pH 8 as functions of time of irradiation. The wavelengths are 497 nm (\blacklozenge), 347 nm (\blacksquare) and 235 nm (\blacktriangle).

negatively charged at low or high zero point charge (zpc), respectively. This behavior can be expected to primarily influence the adsorption of the dye on the catalyst, thus

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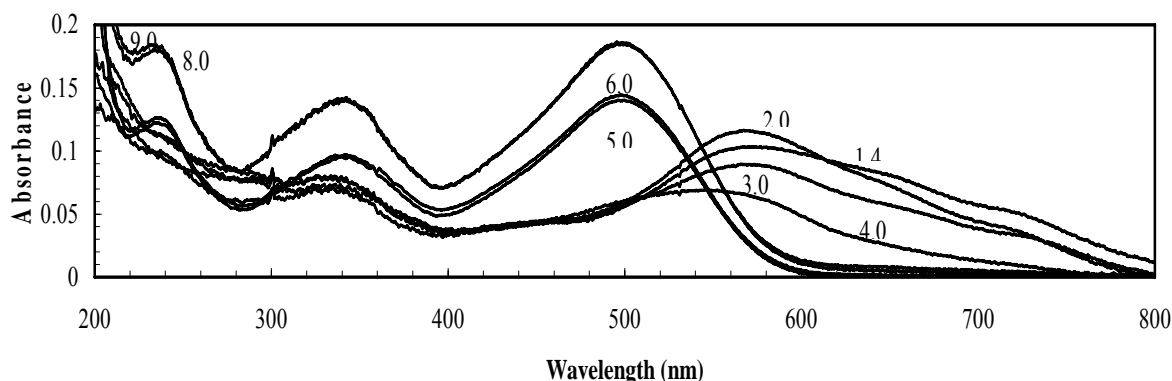
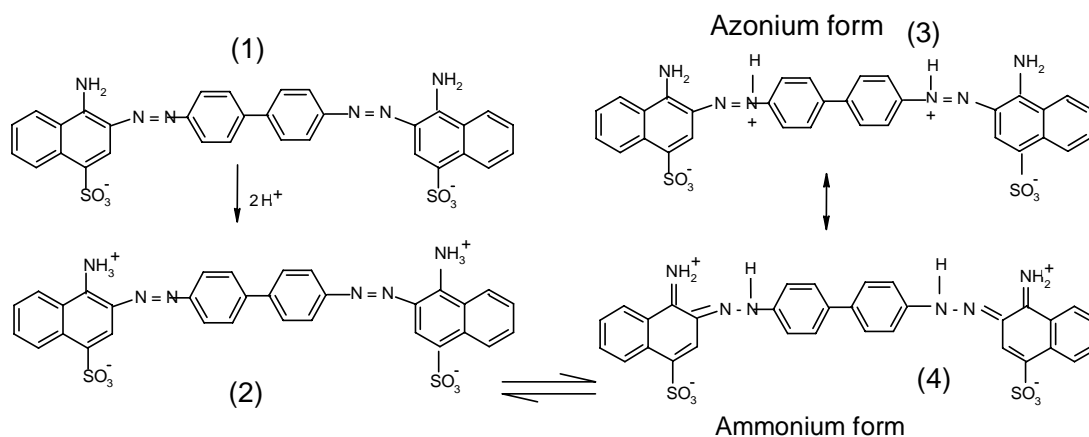


Fig. 11. Absorption spectra of aggregated Congo red aqueous solution (5 ppm) at different pH.



Scheme 2. Protonated of Congo red.

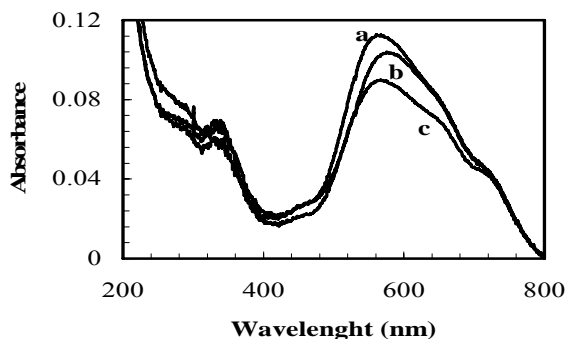


Fig. 12. UV-Vis absorption spectra of Congo red (5 ppm) in high acidic aqueous solutions: (a) pH 0.25, (b) pH 0.37 and (c) pH 1.21.

affecting the overall photocatalytic process. Photocatalytic activity of anionic dyes (mainly sulfonated dyes) such as Congo red reaches a maximum value in lower zero point charge. At $\text{pH} > \text{zpc}$, the surface is negatively charged and repels R-SO_3^- ions [18]. Furthermore, dye molecules in acidic or highly acidic pH ranges tend to aggregate and form tautomerism state. Protonation of Congo red could be occurring at amino or azo nitrogens (see Scheme 2, structures 2 and 3).

Structures 3 and 4 represent two distinct resonance structures [25]. In fact, it has been reported that in protonated azo compounds having amino groups, there is an equilibrium mixture of two tautomers (see Scheme 2, structures 3 and 4). Our experiment showed that photocatalytic degradation of

Congo red in aqueous TiO₂ suspension was not completed in acidic conditions, which can be explained with reference to the aggregation phenomenon of dye molecules.

CONCLUSIONS

The following conclusions could be drawn from the present investigation:

1. According to UV-Vis absorption spectra, no aggregation occurred in Congo red dye solutions in pH's whether neutral or basic.
2. The Photocatalytic efficiency of ZnO was shown to be remarkably greater than that of TiO₂ in degradation of Congo red azo dye.
3. Control experiments demonstrated that both UV light and catalyst were needed for the effective destruction of dye.
4. The photodegradation degree of dye was obviously affected by the initial dye concentration.
5. Efficiency of photocatalytic processes strongly depend upon the pH of the solution and the nature of dye.
6. Finally, it can be concluded that ZnO is an efficient recoverable photocatalyst in Congo red degradation whose nature does not change even if it is used for four times.

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the financial support they received from the Tarbiat Modarres University.

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