

Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst

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Abstract

The potential of a common semiconductor, ZnO, has been explored as an effective catalyst for the photodegradation of C.I. Acid Yellow 23 (AY23). The effects of process parameters such as, catalyst loading, initial dye concentration, light intensity, and pH on the extent of photodegradation have been investigated. Substantial reduction of COD, besides removal of color, was also achieved. A rate equation for the degradation based on Langmuir–Hinshelwood (L–H) model has been proposed. The results show that the adsorption constant (K_{ads}) and rate constant (k_{L-H}) in L–H model are dependent to the light intensity, and increase with increasing the light intensity. With inserting the light intensity parameter to L–H equation, this model can be used for predicting the removal rate at different light intensities and initial concentrations of AY23. A comparison between experimental and calculated apparent reaction rate constants shows that the results obtained from the L–H modified model are in good agreement with experimental data.

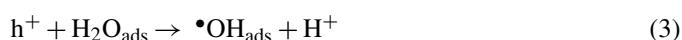
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Keywords: Photocatalysis; Decolorization; C.I. Acid Yellow 23; ZnO; Kinetic

1. Introduction

Wastewater from textile, paper, and some other industries contain residual dyes, which are not readily biodegradable. One of them is tartrazine. C.I. Acid Yellow 23 is an azo dye present in thousands of foods and drugs and has been reported as a possible cause of asthma, urticaria, and angioedema [1]. It also has phototoxic potentials. Adsorption and chemical coagulation are two common techniques of treatment of such wastewater. However, these methods merely transfer dyes from the liquid to the solid phase causing secondary pollution and requiring further treatment [2]. Semiconductor photocatalysis is a newly developed AOP, which can be conveniently applied for the degradation of dye pollutants. Semiconductors (such as TiO_2 , ZnO, Fe_2O_3 , CdS, and ZnS) are important due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band [3]. The biggest advantage of ZnO in comparison with TiO_2 is that it absorbs over a larger fraction of UV spectrum and the corre-

sponding threshold of ZnO is 425 nm. Upon irradiation, valence band electrons are promoted to the conduction band leaving a hole behind (Eq. (1)). These electron–hole pairs can either recombine (Eq. (2)) or interact separately with other molecules. The holes at the ZnO valence band can oxidize adsorbed water or hydroxide ions to produce hydroxyl radicals (Eqs. (3) and (4)). Electron in the conduction band on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (5)). This radical may form organic peroxides or hydrogen peroxide in the presence of organic scavengers (Eqs. (6) and (7)). The hydroxyl radical is a powerful oxidizing agent and attacks to organic compounds and intermediates (Int.) are formed. These intermediates react with hydroxyl radicals to produce final products (P) (Eq. (8)). The mechanism of heterogeneous photocatalysis presented in Fig. 1 [4].



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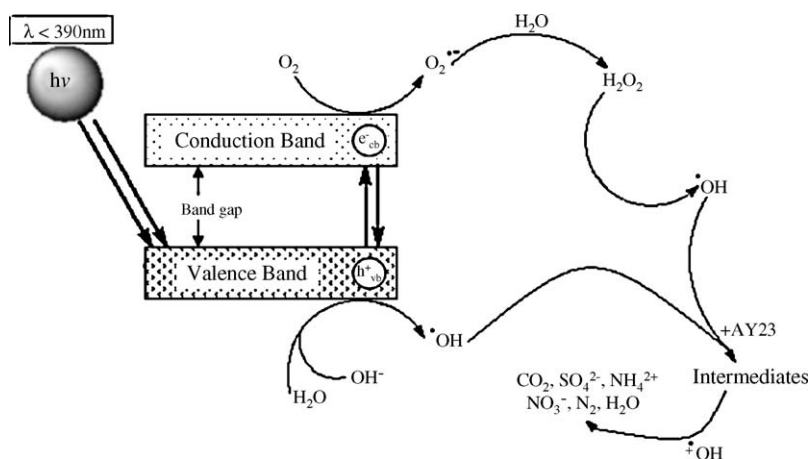
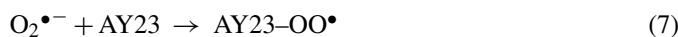
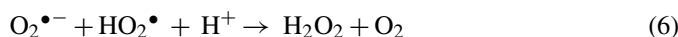


Fig. 1. General mechanism of photocatalysis.



The aim of the present work is to investigate the influence of operational parameters on the decolorization kinetics of AY23 in UV/ZnO process and also relation between L–H model parameters and light intensity.

2. Experimental

2.1. Materials

C.I. Acid Yellow 23 (AY23), a mono azo anionic dye was obtained from ACROS organics (USA). Its chemical structure and other characteristics are listed in Table 1. ZnO, NaOH, and HCl were purchased from Merck (Germany). Solutions were prepared by dissolving appropriate amount of the dye in double distilled water before each experiment.

2.2. Photoreactor

All the experiments were carried out in a batch photoreactor. The radiation source was a UV lamp (30 W, UV-C, $\lambda_{\text{max}} = 254 \text{ nm}$, manufactured by Philips, Holland), which was

placed above a Pyrex 0.5 l reactor. The light intensity in the center of photoreactor was measured by Lux-UV-IR meter (Leybold Co.).

2.3. Procedures

For the photocatalytic degradation of AY23, a solution containing known concentration of the dye and ZnO was prepared and allowed to equilibrate for 30 min in the darkness, then 200 ml of the prepared suspension was transferred into the reactor, then the lamp was switched on to initiate the reaction. During irradiation, the glass reactor mounted on a magnetic stirrer to keep the suspension homogenous and at certain reaction intervals, 10 ml of sample was withdrawn, centrifuged, and the dye concentration was analyzed with a UV–vis spectrophotometer (Ultrospec 2000, England) at 428 nm. A calibration plot based on Beer–Lambert’s law was established by relating the absorbance to the concentration. The changes in the absorption spectra of AY23 at different irradiation times were recorded on a double-beam UV–vis spectrophotometer (Shimadzu 1700) in the wavelength range from 190 to 550 nm. Chemical oxygen demand (COD) was measured by the dichromate reflux method. The Zn^{2+} concentration was measured with atomic absorption (Varian 200).

3. Results and discussion

3.1. Effect of the photocatalyst concentration

Some dyes are degraded by direct UV radiation. Therefore, it should be examined to what extent the AY23 are ‘photolyzed’ if no catalyst was used. Blank experiments were carried out for the dye without catalyst for this purpose. It is also interesting to determine, the minimum amount of catalyst required to decolorize the maximum amount of dye at a particular experimental condition. With an increased catalyst loading from 150 to 750 mg l^{-1} the percent of degradation increased from 49.1 to 92.98 at 60 min irradiation time. After that the increase in catalyst loading did not affect the degradation significantly. Thus, the catalyst loading for maximum degradation of 40 mg l^{-1} of

Table 1
Structure and characteristics of C.I. Acid Yellow 23

Structure	
Other name	Tartrazine
C.I. number	19140
λ_{max} (nm)	428
M_w (g mol^{-1})	534.385

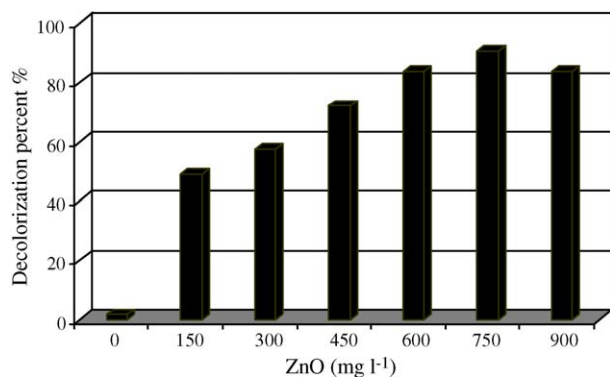


Fig. 2. Effect of ZnO loading on photocatalytic degradation of AY23. $[AY23]_0 = 40 \text{ mg l}^{-1}$, $\text{pH} \cong 7$, $I_0 = 34.2 \text{ W m}^{-2}$.

AY23 was 750 mg l^{-1} under the experimental conditions specified in Fig. 2. The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn increased the number of hydroxyl, and superoxide radicals [2,4]. When the concentration of ZnO catalyst was increased above the limiting value, the degradation rate decreased due to an increase in the turbidity of the suspension and a decrease in UV light penetration as a result of increased scattering effect [2–4].

3.2. Effect of the initial dye concentration

The influence of initial concentration of the dye solution on the photocatalytic degradation is an important aspect of the study. Initial concentrations of AY23 were varied in the range of $20\text{--}50 \text{ mg l}^{-1}$ and the photodegradation percent decreased with increasing initial concentration of the dye solution as shown in Fig. 3. An explanation to this behavior is that as initial concentration increases, more and more organic substances are adsorbed on the surface of ZnO, therefore, the generation of hydroxyl radicals will be reduced since there are only a fewer active sites for adsorption of hydroxyl ions and the generation of hydroxyl radicals. Further, as the concentration of a dye solution increases, the photons get intercepted before they can reach the catalyst surface, hence the absorption of photons by the catalyst decreases, and consequently the degradation percent is reduced [5–7].

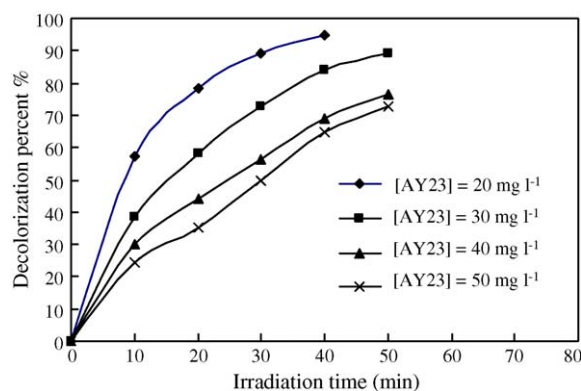


Fig. 3. Effect of the initial dye concentration on photocatalytic degradation of AY23. $\text{pH} \cong 7$, $I_0 = 34.2 \text{ W m}^{-2}$, $[ZnO] = 750 \text{ mg l}^{-1}$.

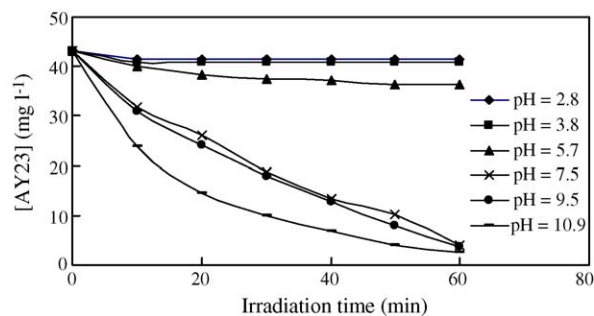


Fig. 4. Effect of initial pH on photocatalytic degradation of AY23. $I_0 = 34.2 \text{ W m}^{-2}$, $[ZnO] = 750 \text{ mg l}^{-1}$, $[AY23]_0 = 40 \text{ mg l}^{-1}$.

3.3. Effect of pH

The interpretation of pH effects on the efficiency of dye photodegradation process is a very difficult task since it has multiple roles. Because of the amphoteric behavior of most semiconductor oxides, an important parameter governing the rate of reaction taking place on semiconductor particle surface is the pH of the dispersions, since, it influences the surface-charge properties of the photocatalysts. Further, industrial effluents may not be neutral. Therefore, the effect of pH on the rate of degradation needs to be considered. Experiments were carried out at pH values of (2.8–10.9) using 40 mg l^{-1} AY23 plus 750 mg l^{-1} ZnO. Fig. 4 shows the time–concentration profiles of degradation of AY23 at various pHs. The extent of photocatalysis increased with increasing pH. The decrease in the photocatalytic degradation at acidic pH may be due to dissolution of ZnO at low pH. The presence of Zn^{2+} was measured at three different pHs. The results indicate that at pH of 7.5 there was no trace of Zn^{2+} , but at pH of 5.2 and 2.5, the amount of above cation was 365 and 430 mg l^{-1} , respectively. This clearly confirms that at acidic medium the dissolution of ZnO would occur. At higher pHs, there were excess of hydroxyl anions, which facilitate photogeneration of hydroxyl radicals [3,8–10].

3.4. Effect of the light intensity

The influence of light intensity on the degradation efficiency has been examined at constant dye concentration (40 mg l^{-1}) and catalyst loading (750 mg l^{-1}). It is evident that the percentage of decolorization and photodegradation increases with increasing the light intensity as shown in Fig. 5. Because the UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [2,7].

3.5. Effect of H_2O_2 concentration

The rate of photocatalytic degradation of organic compounds is significantly improved either in the presence of oxygen or

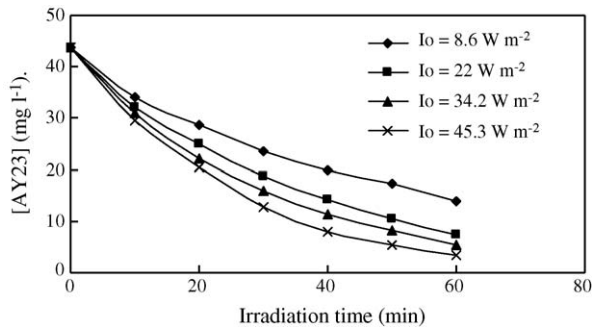
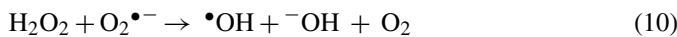
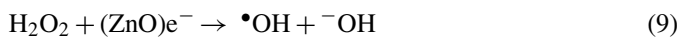
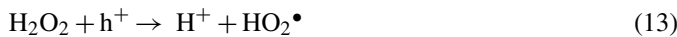
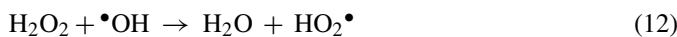


Fig. 5. Effect of the light intensity on photocatalytic degradation of AY23. $\text{pH} \cong 7$, $[\text{ZnO}] = 750 \text{ mg l}^{-1}$, $[\text{AY23}]_0 = 40 \text{ mg l}^{-1}$.

by addition of hydrogen peroxide. The rate of photocatalytic degradation of AY23 first increased when hydrogen peroxide concentration increased and reached to a maximum but above an optimum value increasing H_2O_2 concentration retards the reaction (Fig. 6). This dual effect of H_2O_2 can be explained by radical reaction mechanisms. The added H_2O_2 could accelerate the reaction by producing hydroxyl radicals from scavenging the electrons and absorption of UV-light by the following reactions:



By addition of excess H_2O_2 , it acts as hydroxyl radical or hole scavenger to form the perhydroxyl radicals ($\text{HO}_2\bullet$) which is a much weaker oxidant than hydroxyl radicals [8,9]:



Therefore, high concentration of hydrogen peroxide inhibited the reaction rate of dye degradation by competing with AY23 for available hydroxyl radicals.

3.6. Effects of HCO_3^- and CO_3^{2-}

The presence of other chemicals used in the dye industry has been shown to influence the photocatalytic decolorization and

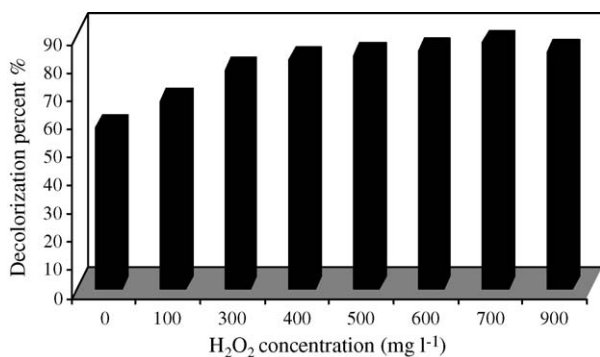


Fig. 6. Effect of hydrogen peroxide concentration on photocatalytic degradation of AY23. $I_0 = 34.2 \text{ W m}^{-2}$, $[\text{ZnO}] = 750 \text{ mg l}^{-1}$, $[\text{AY23}]_0 = 40 \text{ mg l}^{-1}$, $\text{pH} \cong 4.7$, Irradiation time = 30 min.

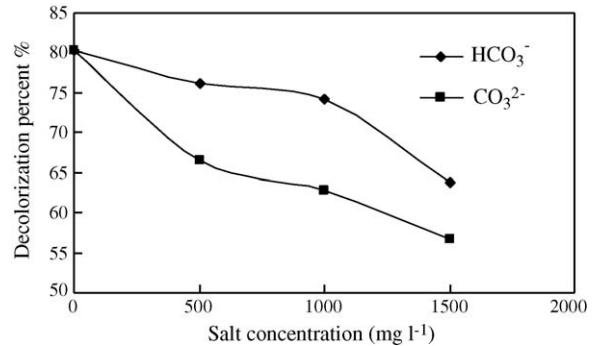
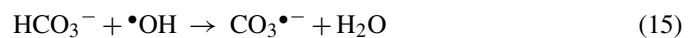


Fig. 7. Effect of HCO_3^- and CO_3^{2-} concentrations on the photocatalytic degradation of AY23. $I_0 = 34.2 \text{ W m}^{-2}$, $[\text{ZnO}] = 750 \text{ mg l}^{-1}$, $[\text{AY23}]_0 = 40 \text{ mg l}^{-1}$, $\text{pH} \cong 7$, irradiation time = 30 min.

degradation efficiency. The effect of presence of common anions such as carbonate and bicarbonate on the photocatalytic decolorization of AY23 is shown in Fig. 7. As can be seen, by increasing the concentration of HCO_3^- and CO_3^{2-} the decolorization percent significantly decreased. This inhibition is undoubtedly due to their ability to act as hydroxyl radical's scavengers by the following reactions [9]:



These ions may also block the active sites on the ZnO surface thus deactivating the catalyst towards the AY23 and intermediate molecules. Although, the generated carbonate radical anion has been shown to be an oxidant itself, but its oxidation potential is less positive than that of the hydroxyl radicals.

3.7. Effect of temperature

Temperature has been proved to be an important aspect when studying the photocatalysis of dyes. The photocatalytic degradation rate of AY23 as a function of temperature was studied in UV/ZnO process. Although the semiconductor photocatalysis is usually not very temperature dependent, but an increase in temperature helped the reaction to compete more efficiently with e^-h^+ recombination and causes an increase in removal reaction rate [7]. Fig. 8 shows the Arrhenius plot of $\ln k_{\text{ap}}$ versus T^{-1} for photocatalytic degradation of AY23 in UV/ZnO process.

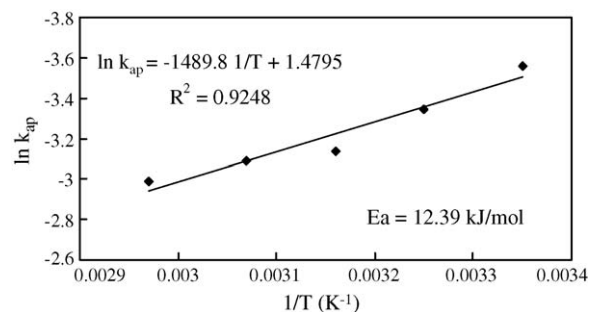


Fig. 8. Effect of temperature on photocatalytic degradation of AY23. $I_0 = 34.2 \text{ W m}^{-2}$, $[\text{ZnO}] = 750 \text{ mg l}^{-1}$, $\text{pH} \cong 7$, $[\text{AY23}]_0 = 40 \text{ mg l}^{-1}$.

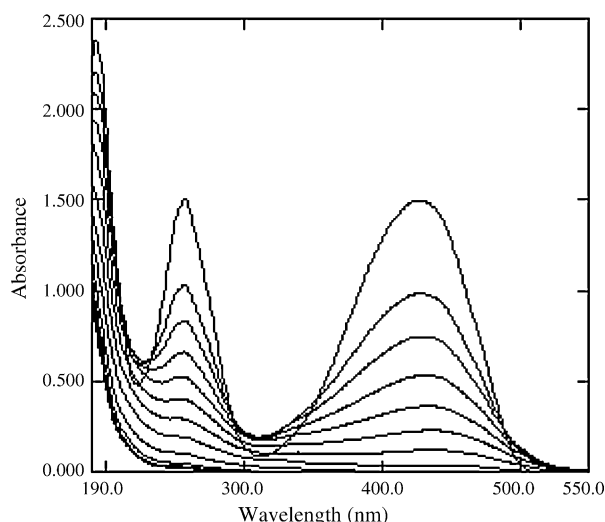


Fig. 9. UV-vis spectral changes of AY23, recorded during the dye degradation at different irradiation times. $I_0 = 34.2 \text{ W m}^{-2}$, $[\text{ZnO}] = 750 \text{ mg l}^{-1}$, $\text{pH} \cong 7$, $[\text{AY23}]_0 = 40 \text{ mg l}^{-1}$.

The slope of this straight line was 1489.8, which corresponds to activation energy of $12.39 \text{ kJ mol}^{-1}$.

3.8. Spectral changes of AY23 and COD measurements during photooxidation

The changes in absorption spectra of AY23 during UV/ZnO process at 10 min irradiation intervals were shown in Fig. 9. The decrease of the absorption peak of AY23 at $\lambda = 428 \text{ nm}$ in Fig. 9 indicates a rapid degradation of azo dye. The decrease is also meaningful with respect to the nitrogen to nitrogen double bond ($-\text{N}=\text{N}-$) of the azo dye, as the most active site for oxidative attack. It is interesting to note from Fig. 9 that the absorption of the visible band at 428 nm decreased with time and that a new band started to form at 225 and 315 nm . After 20 min the band intensity at 225 and 315 nm started to decrease and after 90 min disappeared. This trend suggests that in the first period the polyaromatic rings in AY23 start to degrade, creating mono substituted aromatics thus band at around 225 and 315 nm increases in intensity [11]. After 90 min the bands at 225 , 315 , and 428 nm disappeared.

The COD changes during photocatalytic degradation of AY23 are in agreement with this trend. As can be seen from Fig. 10 the amount of COD increased in the first 30 min of irradiation, which was attributed to the destruction of the AY23 to smaller compounds that are less resistant to chemical oxidation. Finally, almost 50% of the COD was removed after 90 min of irradiation.

4. Kinetic modeling

The photocatalytic oxidation kinetics of many organic compounds have often been modeled with the Langmuir–Hinshelwood equation, which also covers the adsorption properties of the substrate on the photocatalyst surface. This model was developed by Turchi and Ollis [12] and expressed as Eq.

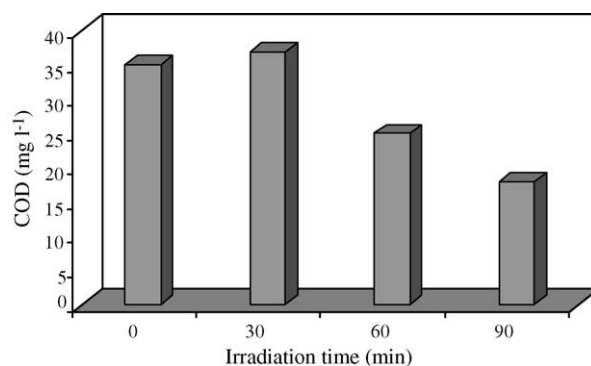


Fig. 10. COD changes vs. irradiation time for photocatalytic degradation of AY23. $I_0 = 34.2 \text{ W m}^{-2}$, $[\text{ZnO}] = 750 \text{ mg l}^{-1}$, $\text{pH} \cong 7$, $[\text{AY23}]_0 = 40 \text{ mg l}^{-1}$.

(16):

$$R = -\frac{d[\text{AY23}]}{dt} = \frac{k_{\text{L-H}}K_{\text{ads}}[\text{AY23}]}{1 + K_{\text{ads}}[\text{AY23}]} \quad (16)$$

where R is the reaction rate ($\text{mg l}^{-1} \text{ min}^{-1}$), $k_{\text{L-H}}$ the reaction rate constant ($\text{mg l}^{-1} \text{ min}^{-1}$), K_{ads} the adsorption coefficient of dye on the ZnO particles ($\text{mg}^{-1} \text{ l}$), and $[\text{AY23}]$ the concentration of dye (mg l^{-1}). Al-Ekabi and Serpone [13] have admitted that the rate must include competitive adsorption by intermediates. Under these reasonable conditions, the Eq. (16) can be written as follows:

$$R = -\frac{d[\text{AY23}]}{dt} = \frac{k_{\text{L-H}}K_{\text{ads}}[\text{AY23}]}{1 + K_{\text{ads}}[\text{AY23}] + \sum K_i C_i} \quad (17)$$

In this equation, K_i and C_i are the adsorption equilibrium constant and concentration for intermediates, respectively. Beltran-Heredia et al. [14] made the following assumption:

$$K_{\text{ads}}[\text{AY23}] + \sum K_i C_i = K_{\text{ads}}[\text{AY23}]_0 \quad (18)$$

In this equation, $[\text{AY23}]_0$ is the initial concentration of AY23. By substituting Eq. (18) in to Eq. (17), we obtain:

$$R = -\frac{d[\text{AY23}]}{dt} = \frac{k_{\text{L-H}}K_{\text{ads}}[\text{AY23}]}{1 + K_{\text{ads}}[\text{AY23}]_0} = k_{\text{ap}}[\text{AY23}] \quad (19)$$

which

$$k_{\text{ap}} = \frac{k_{\text{L-H}}K_{\text{ads}}}{1 + K_{\text{ads}}[\text{AY23}]_0} \quad (20)$$

Eq. (19) shows a pseudo-first order reaction with respect to the AY23 concentration. The semi-logarithmic graphs of the concentration of AY23 in the presence of different concentrations of ZnO versus irradiation time yield straight lines indicating pseudo-first order reaction. The apparent reaction rate constants (k_{ap}) for photocatalytic degradation of AY23 were evaluated from experimental data (Fig. 11) using a linear regression. In all cases, R^2 (correlation coefficient) values are higher than 0.99, which confirm the proposed kinetics for decolorization of AY23 in this process. The constants $k_{\text{L-H}}$ and K_{ads} in L–H model were obtained with fitting k_{ap} to $[\text{AY23}]_0$ at different light intensities using the software package Matlab (Version 6.5) and were listed in Table 2.

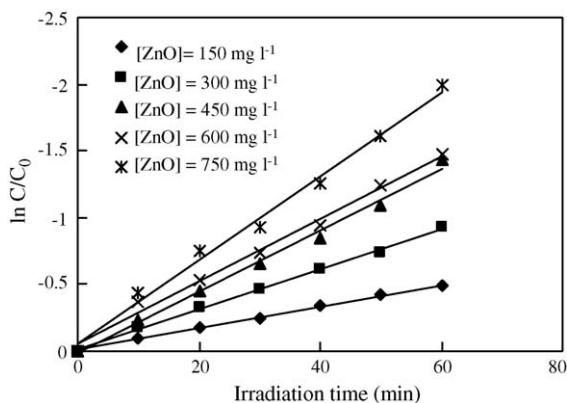


Fig. 11. Derivation of the pseudo-first order rate constants of AY23 in the UV/ZnO process by linear regression. $[AY23]_0 = 40 \text{ mg l}^{-1}$, $\text{pH} \cong 7$, $I_0 = 34.2 \text{ W m}^{-2}$.

Table 2
Langmuir–Hinshelwood equation constants for decolorization of AY23 (40 mg l^{-1}) in the presence of ZnO (750 mg l^{-1}) at different UV-light intensities

I_0 (W m^{-2})	k_{L-H} ($\text{mg l}^{-1} \text{ min}^{-1}$)	K_{ads} (mg^{-1})
8.6	0.913	3.15
19.2	1.356	21.8
34.2	1.490	73.99
45.3	1.796	113.0

In Eq. (16) proposed by Turchi and Ollis [12], K_{ads} is independent of light intensity because it reflects the adsorptive affinity of a substrate on the catalyst surface. However, Meng et al. [15] observed that K_{ads} is light intensity-dependent for photocatalytic degradation of para-chlorobenzoate with TiO_2 as photocatalyst. We have observed that constants k_{L-H} and K_{ads} are light intensity-dependent as follows (Fig. 12):

$$K_{ads} = 0.12 \times I_0^{1.79} \quad (R^2 = 0.995) \quad (21)$$

$$k_{L-H} = 0.42 \times I_0^{0.37} \quad (R^2 = 0.991) \quad (22)$$

Increasing K_{ads} with increasing the light intensity reflects the fact that the adsorption tendency of AY23 is enhanced by irradiation of the photocatalyst surface.

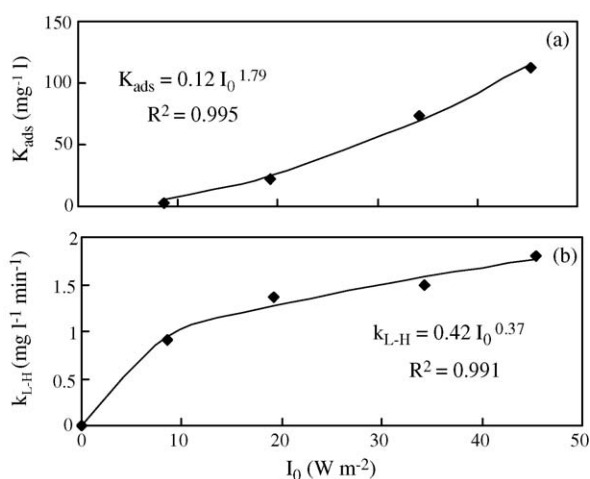


Fig. 12. Relation between K_{ads} (a) and k_{L-H} (b) in L-H model with light intensity.

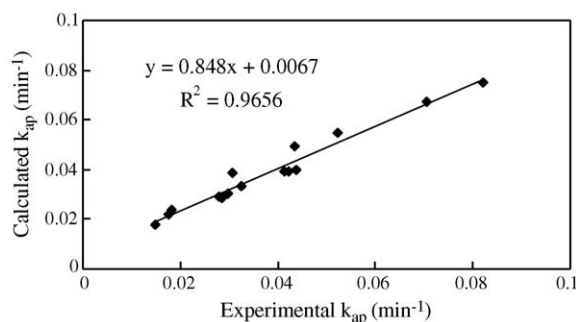


Fig. 13. A comparison between experimental and calculated apparent reaction rate constants obtained from the L–H modified model.

By substituting Eqs. (21) and (22) in to Eq. (20), we obtain:

$$k_{ap} = \frac{0.05 \times I_0^{2.16}}{1 + 0.12 \times I_0^{1.79} [AY23]_0} \quad (23)$$

For evaluation of Eq. (23) at predicting of k_{ap} at different light intensities and initial concentrations of AY23, a comparison between experimental and calculated k_{ap} for decolorization of AY23 with UV/ZnO process was shown in Fig. 13. From this plot, it can be seen that the results obtained from the model are in good agreement with the experimental data.

5. Conclusions

Effective destruction of AY23, a mono azo dye, is possible by photocatalysis in the presence of ZnO suspension and UV light. The kinetic of the photocatalytic decolorization follows a Langmuir–Hinshelwood model and depends on several factors such as, dye concentration, catalyst loading, light intensity, and pH. The results show that the adsorption constant K_{ads} and rate constant k_{L-H} in L–H model increases with increasing light intensity. The modified L–H model can be used for predicting apparent reaction rate constant at different light intensities.

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