Effect of operational parameters on decolorization of Acid Yellow 23 from wastewater by UV irradiation using ZnO and ZnO/SnO$_2$ photocatalysts

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ABSTRACT

Advanced Oxidation Processes (AOPs) have been used as emerging wastewater treatment technologies which can effectively handle various hazardous organics in wastewater and groundwater. This study examined the photodecolorization of azo dyes in aqueous solution by combined UV, individual and coupled photocatalysts. The model substrate employed in this work was C.I. Acid Yellow 23 (AY23) and the ZnO and ZnO/SnO$_2$ were utilized as the photocatalysts. A 30 W UV lamp was the source of UV-radiation in a batch reactor. Photodecolorization efficiency was small when the photolysis was carried out in the absence of ZnO and it was also negligible in the absence of UV light. The effects of various parameters such as catalysts loading, initial dye concentration, radiation intensity, pH, gap size and catalysts ratio on the dye removal have been investigated. The results showed that the removal efficiency of AY23 is optimal with 1.4 cm gap size, 40 mg L^{-1} of azo dye concentration and the catalysts amounts of ZnO and SnO$_2$ were adjusted to be 700 mg L^{-1} and 200 mg L^{-1}, respectively. Accordingly, it could be stated that the complete decolorization of color, after selecting desired operational parameters could be achieved in about 50 min.

1. Introduction

Textile industry produces large quantities of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Azo dye, such as Acid Yellow 23 (AY23), are widely used in the textile industry [1,2]. Various chemical and physical processes, such as chemical precipitation and filtration, coagulation, electrocoagulation, adsorption on activated carbon, and etc. have been applied to remove color from textile effluents [3,4]. One difficulty with these methods, is that they are not destructive but only transfer the contamination from one phase to another, therefore, a new and different kind of pollution is faced which calls for further treatment [5,6]. In recent years, an alternative to non-destructive methods is "advanced oxidation processes" (AOPs), based on the generation of very reactive species such as hydroxyl radicals that quickly and non-selectively oxidizes a broad range of organic pollutants [7–10]. AOPs include photocatalysis systems such as combination of a semiconductor (TiO$_2$, ZnO, Fe$_2$O$_3$, etc.) and UV light. Semiconductors are important due to their electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band and an empty conduction band [11]. Photo-catalytic oxidation is an alternative method for the complete

degradation of azo dyes [12–14]. It has been established that the photocatalytic degradation of organic matter in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an electron-hole pair on the surface of the catalyst (e.g. ZnO) as shown in Eq. (1). The high oxidation potential of the hole (h_{VB}^+) in the catalyst permits the direct oxidation of organic matter (dye) into reactive intermediates (Eq. (2)). Very reactive hydroxyl radical can also be formed either by the decomposition of water (Eq.(3)) or by the reaction of the hole with OH$^-$ (Eq. (4)). The hydroxyl radical is an extremely strong, non-selective oxidant that leads to the degradation of organic chemicals [1,15–18].

$$ZnO + h\upsilon \rightarrow \left(e_{CB}^- + h_{VB}^+ \right) \tag{1}$$

$$h_{VB}^+ + \text{dye} \rightarrow \text{oxidation of the dye} \tag{2}$$

$$h_{VB}^+ + H_2O \rightarrow H^+ + {}^\bullet OH \tag{3}$$

$$h_{VB}^+ + OH^- \rightarrow {}^\bullet OH \tag{4}$$

Electron in the conduction band (e_{CB}^-) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (6)). In the presence of organic scavengers, this radical may form organic peroxides (Eq. (7)) or hydrogen peroxide (Eq. (8)).

$$e_{CB}^- + O_2 \rightarrow O_2^- \tag{5}$$

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$$\overset{\bullet}{O_2^-} + dye \rightarrow dye-OO^{\bullet} \tag{6}$$

$$\overset{\bullet}{O_2^-} + HO_2^{\bullet} + H^+ \rightarrow H_2O_2 + O_2 \tag{7}$$
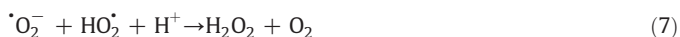
Electrons in the conduction band are also responsible for the production of hydroxyl radicals, which have been indicated as the primary cause of organic matter mineralization as indicated in Eq. (8) [1,19].

$$^{\bullet}OH + dye \rightarrow Int. \rightarrow P \tag{8}$$
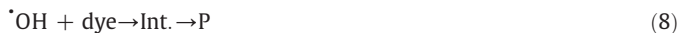
However, the rapid recombination of photo produced electron and holes in semiconductors significantly reduces the efficiency of photocatalytic reaction, thus limiting its application [20]. To improve the photocatalytic efficiency of semiconductor an inter-catalyst electron transfer process is proposed which couples two semiconductors with different redox energy levels to increase charge separation for the corresponding conduction and valence bands [20]. Inter-catalyst irreversibly transfers electrons from the photo-activated semiconductor to the non-photocativated semiconductor and transferres holes from the non-photoactivated semiconductor to the photoactivated semiconductor [20,21]. The efficiency of photocatalytic reactions can thus be enhanced. The aim of this study is to apply ZnO and SnO₂ to decolorize Acid Yellow 23 and compare the photodecolorization efficiency of single semiconductor and coupled semiconductor systems. The effect of UV irradiation, pH, the amount of photocatalyst, gap size and the initial concentration of pollutant on the photodecolorization efficiency was examined.

2. Experimental

2.1. Materials

C.I. Acid Yellow 23 (AY23), a mono azo anionic dye was obtained from ACROS organic (USA) and used without further purification. Structure of Acid Yellow 23 is given in Fig. 1. ZnO, HCl and NaOH were purchased from Merck (Germany). SnO₂ was purchased from Fluka (Switzerland). All Solutions were prepared by dissolving appropriate amount of the dye in double distilled water.

2.2. Photoreactor and light source

All experiments were carried out in a batch photoreactor. It consists of a glass container (500 mL) and the radiation source was a UV lamp (30 W, UV-C, $\lambda_{max} = 254$ nm, manufactured by Philips, Holland) which was located above the surface of the dye solution. The total intensity reaching the slurry solution was measured using a Lux-UV-IR meter (Leybold Co. Germany).

2.3. Procedures

For the photodecolorization of AY23, a solution containing known concentration of dye and photocatalyst (ZnO or SnO₂ and/or ZnO/SnO₂) was allowed to equilibrate for 30 min in the darkness then 200 mL of the prepared suspension was transferred into a pyrex reactor. The suspension pH values were adjusted at a desired level using a dilute of NaOH and HCl. The pH values were measured using
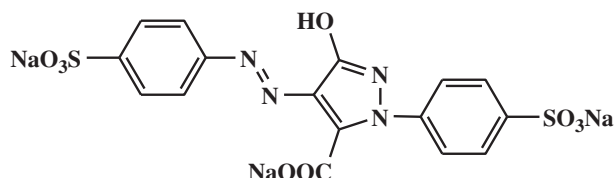
Fig. 1. Structure of C.I. Acid Yellow 23 (C.I. no. 19140).

Table 1
Operating conditions of experiments.

Parameters	Values
ZnO and SnO₂ amounts (mg L^{-1})	150–1050
AY23 initial concentrations (mg L^{-1})	20–50
Light intensity (W m^{-2})	8–40
Gap size (cm)	1.4–3.5
pH	2.28–9.52

pH meter (pH-meter 140 corning). After attaining the equilibrium, the UV lamp was switched on to initiate the reaction. The glassware was covered with aluminum foil during the tests to minimize the exposure of samples to light and to prevent any undesired side-reactions. During irradiation, agitation was maintained to keep the suspension homogenous by a magnetic stirrer. At certain reaction intervals, 2 mL of sample was withdrawn, centrifuged at 8000 rpm to remove any suspended solid and concentration of AY23 was determined with a spectrophotometer (Ultrospect 2000, Biotech Pharmacia, England) at 428 nm. Calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration. Coupled semiconductor system was prepared using appropriate amount of each semiconductor as slurry by mixing them for one hour. The temperature of the solution during the experiments was kept at 25 ± 1 °C in a circulating water bath. By this method conversion percent of AY23 can be obtained at different intervals. The operational conditions of experiments have been summarized in Table 1. The equation used to calculate the color removal efficiency in the treatment experiments was:

$$Color\ Removal\ \% = \frac{C_{\circ} - C}{C_{\circ}} \times 100 \tag{9}$$

where $C_{\circ}$ and C are the initial and final concentrations of the dye (mg L^{-1}) in the solution, respectively.

3. Results and discussion

3.1. Effect of UV irradiation on AY23 decolorization using ZnO and SnO₂ photocatalysts

Figs. 2 and 3 show the effect of UV irradiation on photodecolorization of AY23. It can be seen from Fig. 2 that in the presence of both ZnO and light, 45.4% of the dye was decolorized at the irradiation time of 60 min. This was contrasted with 3.4% decolorization for the same
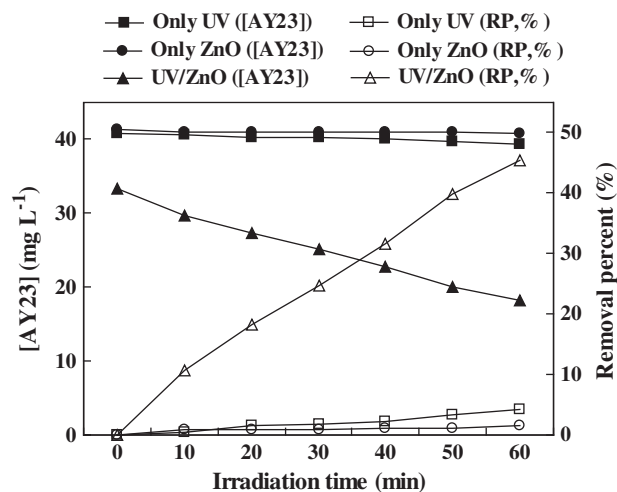
Fig. 2. Effect of UV light and ZnO on photocatalytic decolorization of AY23. [AY23] = 40 mg L^{-1}, [ZnO] = 150 mg L^{-1}, LI = 40 W m^{-2}, pH neutral.

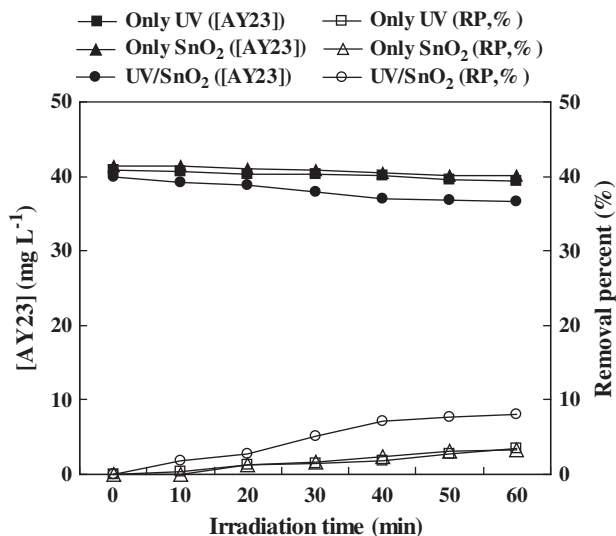**Fig. 3.** Effect of UV light and SnO$_2$ on photocatalytic decolorization of AY23. [AY23] = 40 mg L^{-1}, [SnO$_2$] = 150 mg L^{-1}, LI = 40 W m^{-2}, pH neutral.

experiment performed in the absence of ZnO and the negligible 1.5% when the UV lamp had been switched off and the reaction was allowed to continue in the darkness. These experiments demonstrated that both UV light and photocatalysts were needed for the effective decolorization of AY23. As can be seen from Fig. 3 SnO$_2$ had not any effect on the decolorization of AY23. Accordingly, in comparison with the ZnO, SnO$_2$ is a weaker photocatalyst and the formation of an electron-hole pair on the surface of catalyst could not occur effectively on the surface of SnO$_2$.

3.2. Effect of photocatalysts concentration on AY23 decolorization

Effect of catalysts loading on decolorization of AY23 was investigated using ZnO and SnO$_2$ from 150 to 1050 mg L^{-1} keeping other parameters fixed. The results are shown in Figs. 4 and 5. It can be seen from Fig. 4 that during 50 min of irradiation, the removal percent was increased to 99.99% using ZnO (with the concentrations of 900 mg L^{-1}) from 26.85% with the catalyst concentration of 150 mg L^{-1} and after that decreased. The similar results were obtained with SnO$_2$ catalysts. According to Fig. 5, the removal percent was increased with increasing SnO$_2$ concentrations up to 900 mg L^{-1} and then the increase in catalysts loading does not affect the decolorization significantly. This observation can be explained in terms of availability of active sites on the catalysts surface and the penetration of UV light into the suspension. The total active surface area increases with increasing catalysts dosage. At the same time, due to an increase in the turbidity of the suspension, there is
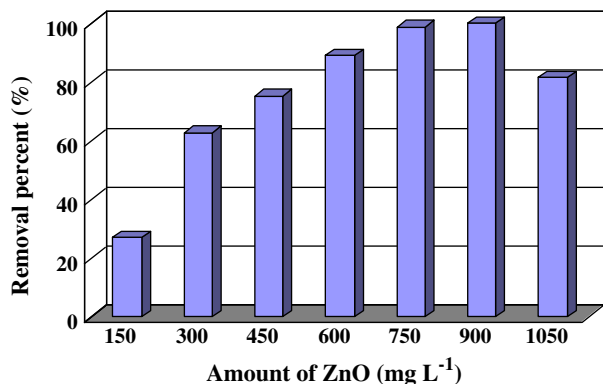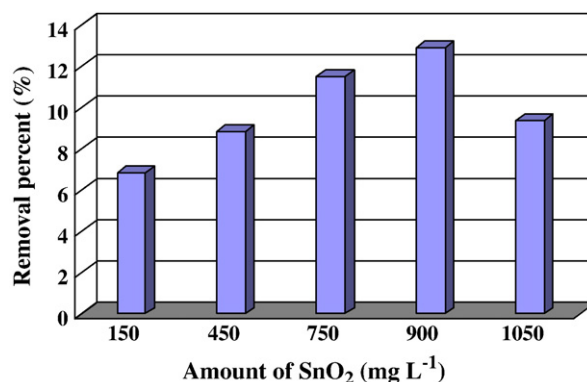

Fig. 5. Effect of SnO$_2$ amount on photodecolorization efficiency of AY23 at irradiation time of 50 min. [AY23] = 40 mg L^{-1}, LI = 40 W m^{-2}, pH neutral.

a decrease in UV light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreases. Further, at high catalyst loading, it is difficult to maintain the suspension homogenous due to catalysts agglomeration which decreases the number of active sites [1,16,22,23]. Since the most effective decomposition of AY23 was observed with 900 mg L^{-1} of photocatalysts, the other experiments were performed in this concentration of catalysts. According to the results obtained from Sections 3.1 and 3.2, due to the weak photocatalysis properties of SnO$_2$, the experiments in Sections 3.3 and 3.4 were carried out only with ZnO.

3.3. Effect of initial dye concentration on AY23 decolorization

From an application point of view, dependence of removal efficiency on initial dye concentration is very important. The effect of this parameter on the degree of photodecolorization was studied by varying the initial concentration over a range of 20–50 mg L^{-1} at ZnO catalyst loading of 900 mg L^{-1}. The results are illustrated in Fig. 6. It can be observed that the photodecolorization conversion of AY23 decreases with an increase in the initial concentration of AY23. The presumed reason is that when the initial concentration increases, more and more dye molecules are adsorbed on the surface of ZnO. Therefore, there are only a fewer active sites for adsorption of hydroxyl ions so the generation of hydroxyl radicals will be reduced. Further, as the concentration of a dye solution increase, the photons get intercepted before they can reach the catalyst surface, hence the adsorption of photons by the catalyst decreases and consequently the decolorization percent is reduced [9,23–25].
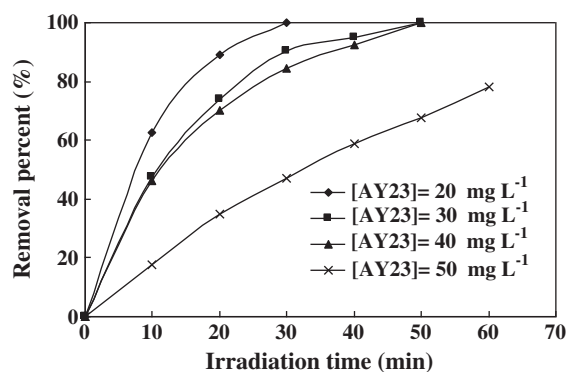

Fig. 4. Effect of ZnO amount of photodecolorization efficiency of AY23 at irradiation time of 50 min. [AY23] = 40 mg L^{-1}, LI = 40 W m^{-2}, pH neutral.

Fig. 6. Effect of initial dye concentration on photocatalytic decolorization of AY23. [ZnO] = 900 mg L^{-1}, LI = 40 W m^{-2}, pH neutral.
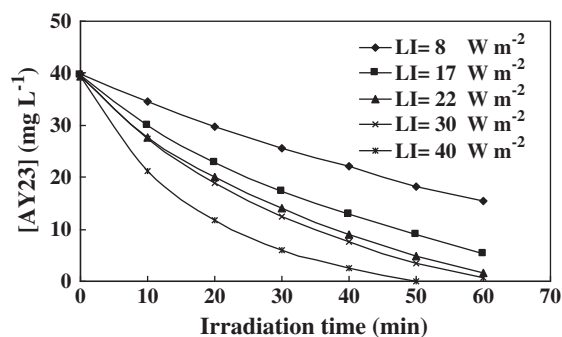
Fig. 7. Effect of light intensity on photocatalytic decolorization of AY23. [AY23] = 40 mg L^{-1}, [ZnO] = 900 mg L^{-1}, pH neutral.

3.4. Effect of light intensity on AY23 decolorization

The influence of UV-light intensity on the decolorization of AY23 has been monitored by varying the UV-light intensity from 8 to 40 W m^{-2} at a constant dye concentration (40 mg L^{-1}) and catalyst (ZnO) loading (900 mg L^{-1}). It appears from Fig. 7, that with increasing the light intensity the decolorization rate increases. 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 decolorization increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [1,19,24].

3.5. Effect of single and coupled catalysts on AY23 decolorization

In order to use suitable quantity of catalysts for an efficient photodecolorization, two sets of experiments were carried out. As shown in Fig. 8, the difference between removal efficiency of ZnO alone and coupled photocatalysts (ZnO/SnO$_2$) was not significant. The optimum amount of the above photocatalysts was found to be 900 mg L^{-1} for both photocatalysts individually. For coupling catalysts, 450 mg L^{-1} of each was mixed to form a slurry combination and used in the same condition to compare them. The increase in catalyst weight up to 900 mg L^{-1} increases the dye decolorization sharply which is due to an increase in the number of adsorbed dye molecules and also the increase in the density of catalyst in the area of irradiation. Beyond, this concentration, the decolorization starts to decrease which is attributed to the enhancement of light reflectance by the catalysts and decrease in light penetration [26]. In order to examine the coupled form of photocatalysts in the decolorization process, 450 mg L^{-1} of each catalyst was employed. As it can be seen
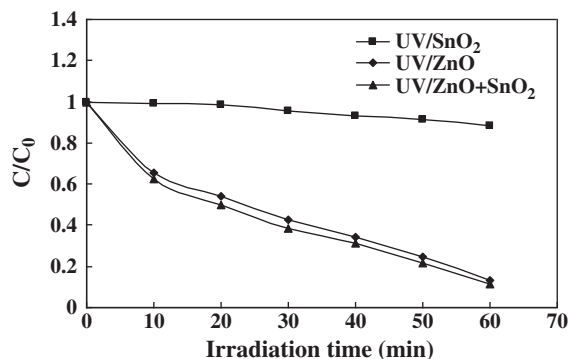

Fig. 8. Comparison of photocatalytic activity of ZnO, SnO$_2$ and [ZnO]/[SnO$_2$]. [AY23] = 40 mg L^{-1}, [ZnO] = 900 mg L^{-1}, [SnO$_2$] = 900 mg L^{-1}, [ZnO]/[SnO$_2$] = (450/450) mg L^{-1}, LI = 30 W m^{-2}, pH neutral.
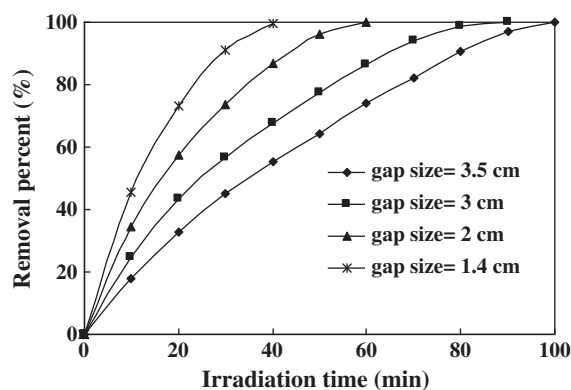

Fig. 9. Effect of gap size on the photodecolorization activity of AY23 vs. irradiation time at different gap size. [AY23] = 40 mg L^{-1}, LI = 40 W m^{-2}, [ZnO]/[SnO$_2$] = (450/450) mg L^{-1}, pH neutral.

from Fig. 8, there was no significant difference between UV/ZnO and UV/ZnO + SnO$_2$ systems and SnO$_2$ did not play any role in the process [20].

3.6. Effect of gap size on the AY23 decolorization

In the previous section, combination of photocatalysts did not improve decolorization rate as expected. In this set of experiments, four different gap sizes (thickness of the solution) were applied to the decolorization of C.I. AY23 dye using 450 mg L^{-1} of ZnO and 450 mg L^{-1} of SnO$_2$. In Fig. 9, the decolorization percentage as a function of the UV irradiation time is illustrated for each gap size. The highest removal percentage was obtained with the smallest gap size (1.4 cm). As we observe, 99% of color removal was obtained in about 40 min for an irradiation time, whereas 55% of the color removal was obtained in the gap size of 3.5 cm. It seems obvious that as thickness of solution reduces light easily penetrates and hydroxyl radicals act efficiently without being scavenged.

3.7. Effect of pH values on AY23 decolorization

Because of the amphoteric behavior of most semiconductor oxides, an important parameter governing the rate of reaction taking place on semiconductor catalyst surfaces is the pH of the dispersions; since, it influences the surface- charge- properties of the photocatalysts [27]. Since industrial effluents may not be neutral, the effect of pH on the rate of decolorization needs to be considered. Experiments were carried out at pH values of 2.28–9.52, using 40 mg L^{-1} AY23 solutions along with 450 mg L^{-1} of ZnO and 450 mg L^{-1} of SnO$_2$. The pH of dye solutions was adjusted by HCl or NaOH before irradiation. Fig. 10
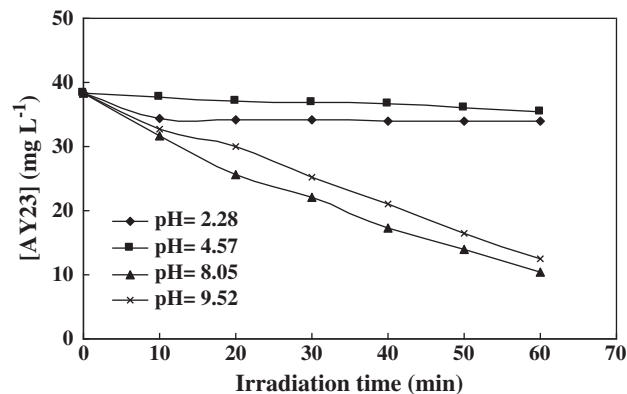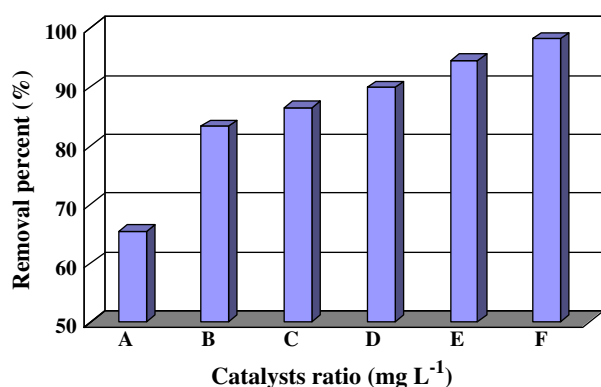

Fig. 10. Effect of pH on photodecolorization efficiency of AY23 at different irradiation time. [AY23] = 40 mg L^{-1}, [ZnO]/[SnO$_2$] = (450/450) mg L^{-1}, LI = 40 W m^{-2}.

Fig. 11. Effect of the catalysts ratio and comparison of UV/ZnO, with UV/ZnO + SnO$_2$ processes during. (A) [ZnO] = 225 mg L^{-1}, (B) [ZnO]/[SnO$_2$] = 175/50 mg L^{-1}, (C) [ZnO] = 450 mg L^{-1}, (D) [ZnO]/[SnO$_2$] = 350/100 mg L^{-1}, (E) [ZnO] = 900 mg L^{-1}, (F) [ZnO]/[SnO$_2$] = 700/200 mg L^{-1}, Irradiation time = 30 min, [AY23] = 40 mg L^{-1}, LI = 30 W m^{-2}, pH neutral.

shows the degree of photodecolorization of AY23 at a fixed reaction time (60 min). The extent of photocatalysis increased with increase in pH and the decrease in the photocatalytic decolorization at acidic pH may be due to dissolution of ZnO, SnO$_2$ at low pH. At higher pHs there was excess of hydroxyl anions, which facilitate photogeneration of hydroxyl radicals [25,28–30]. In this study pH of 8.05 was found to be the desired pH under the experimental conditions. The initial and final pH of the solution were measured and there was no considerable change.

3.8. Effect of the catalysts ratio and comparison of UV/ZnO, with UV/ZnO + SnO$_2$ processes

Fig. 11 indicates that the decolorization of aqueous AY23 increased with the inter-catalyst electron transfer effect. In Section 3.5 combinations of photocatalysts at same ratios did not improve decolorization rate as expected. But changing the ratios increased the removal percent using coupled photocatalysts instead of single one. Further experiments were carried out using coupled photocatalyst in different ratios. The best results were achieved when the ratio of ZnO to SnO$_2$ was kept at 7:2. Three sets of experiments using coupled photocatalyst in slurry conditions were examined, keeping the ratio of ZnO to SnO$_2$ at 7:2. In these experiments, UV/ZnO + SnO$_2$ systems consisted of (700/200) mg L^{-1}, (350/100) mg L^{-1} and (175/50) mg L^{-1} and after 30 min of irradiation, decolorization percent of 98, 89 and 83 was obtained, respectively. Comparison of these findings, with those of single ZnO, where decolorization percent was 94, 86 and 65 after the same irradiation time, revealed that coupled system could enhance the photodecolorization rate. The rate–determining step in the photodecolorization process is speculated to be the reduction of oxygen by the electrons trapped on the photocatalyst surface to produce reduced species [31–34] Failure to scavenge electrons using a sacrificial electron acceptor promotes charge recombination, and hence reduces catalyst photoactivities. The difference between the conduction band of SnO$_2$ and that of ZnO enables the former to act as a sink for the photogenerated electrons. The holes move opposite to the electrons, and photo generated holes can be trapped within the ZnO and thus increase charge separation efficiency. SnO$_2$ in coupled photocatalyst system (ZnO + SnO$_2$) plays an important role in photogenerated electron acceptance. The improvement of charge separation achieved by coupling two photocatalyst systems with different energy levels increases the rate of photocatalytic decolorization. Several researchers have shown that the photocatalytic activity of the coupled semiconductor was higher than that of single semiconductor system [12,20,21,35].
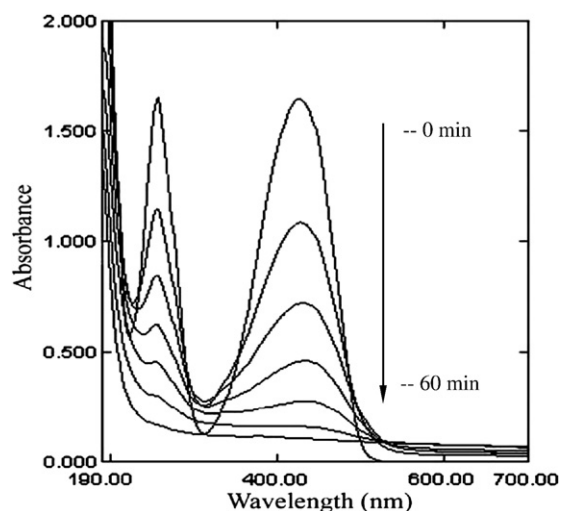
Fig. 12. UV–vis spectra changes of AY23 solution during irradiation time in the presence of ZnO and SnO$_2$. [AY23] = 40 mg L^{-1}, [ZnO]/[SnO$_2$] = (700/200) mg L^{-1}, LI = 30 W m^{-2}, pH neutral.

3.9. Spectral changes of AY23 observed during photodecolorization

Absorption spectra of the dye solution during irradiation are shown in Fig. 12. The maximum absorption wavelength (λ_{max}) for C.I. Acid Yellow 23 dye was determined to be 428 nm. This peak accounts for the yellow color of solutions and can be attributed to the $n-\pi^*$ transition of the non-bonding nitrogen electrons to the anti bonding π^* group orbital of the double bond system and it is used to monitor the decolorization of dye. In the UV region there is a second group of bonds, with increasing absorbency towards lower wavelength at 254 nm, a characteristic of aromatic rings. The decrease of the absorption peak of AY23 at λ_{max} = 428 nm indicated a rapid degradation of the azo dye. Complete decolorization of dye was observed after 50 min of irradiation time.

4. Conclusions

The results presented in this paper indicated that UV/ZnO and UV/ZnO + SnO$_2$ processes could be efficiently used to decolorize the AY23. ZnO and UV light had a negligible effect when they were used on their own. The results indicate that at the ratio of 7:2 (ZnO:SnO$_2$) the decolorization was more efficient than single ZnO. SnO$_2$ in the coupled semiconductor system (ZnO + SnO$_2$) is important in accepting the photogenerated electrons. The improved charge separation resulting from coupling two semiconductor systems with different energy levels enhances the rate of photocatalytic decolorization. The results indicated that the degree of decolorization of AY23 was obviously affected by illumination time, pH, gap size and photocatalyst amount. The decolorization efficiency has been generally, found to increase with an increase in catalysts loading up to an optimal value, pH and UV light intensity, decrease in initial dye concentration and gap size. ZnO and SnO$_2$ cannot be used in acidic solution. The complete decolorization, after selecting the desired operational parameters could be achieved in 50 min. It was found that the amount of both photocatalysts were 900 mg L^{-1}, with dye concentration of 40 mg L^{-1}.

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