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Effect of dye aggregation and azo–hydrazone tautomerism on the photocatalytic degradation of Solophenyl red 3BL azo dye using aqueous TiO_2 suspension

Mohammad Hossein Habibi *, Ali Hassanzadeh, Asghar Zeini-Isfahani

Department of Chemistry, University of Isfahan, Hezar Jerib Street, Isfahan 81745-73441, Iran

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Abstract

Aggregation of Solophenyl red 3BL (C.I. Direct 80) polyazo dye in aqueous solution was investigated using UV–visible and infrared spectroscopy techniques. The results showed a J-aggregate feature in highly acidic aqueous solutions with a red shift compared to monomer in the UV–visible absorption spectra which is due to dimer molecules. Infrared spectra showed that the carbonyl functional group stretch band of the dye molecule was eliminated in highly acidic aqueous solutions which can be related to intermolecular H-bonding. Photocatalytic degradation of Solophenyl red 3BL in aqueous TiO_2 suspension under UV light irradiation in different acidity conditions was also investigated, the results showed that the complete mineralization occurs in low acidic, neutral and basic aqueous solutions but in the highly acidic solutions incomplete photocatalytic degradation was observed which can be related to the aggregated form of 3BL dye molecule. Further studies showed that azo–hydrazone tautomerism did not have any significant effect on the photocatalytic degradation of Solophenyl red 3BL in aqueous solution.

Keywords: Photocatalytic degradation; Aggregation; Azo–hydrazone tautomerism; Solophenyl red 3BL (C.I. Direct 80); TiO_2

1. Introduction

Dye (in particular azo dyes) molecules have extensively been used in industry for applications such as textiles, papers, leathers, gasoline, additives, foodstuffs, cosmetics, laser materials, xerography, laser printing, write-once-read-many-times (WORM) memory systems and so on [1–6]. Aggregation is one of the features of dyes in solution and ionic dyes tend to aggregate in diluted solutions, leading to dimer formation and sometimes even higher order aggregates [7–17]. The aggregation of dyes in aqueous solution is of extreme importance in biological, colloid, surface, textile, photographic and analytical chemistry. Aggregation of dyes is strongly affected by dye concentration and structure, ionic strength, temperature and presence of organic solvents or surfactants [7]. The aggregation may increase with an increase of dye and/or surfactants concentration or ionic strength; it will decrease with temperature rising or organic solvents and/or surfactants adding; addition to the dye structure of ionic solubilizing groups (such as sulfonate group) will decrease aggregation [7], whereas the inclusion of long alkyl chains increases aggregation because of higher hydrophobic interaction in solution. Furthermore, dye molecules with phenyl groups can adopt a planar structure and readily tend to form intermolecular interactions that facilitate permanent aggregation under some experimental conditions [5]. In order to determine the mode of aggregation, the aggregation constant in equilibrium and the aggregation number, the aggregation of dyes have been investigated

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* Corresponding author. Tel.: +68 311 7932707; fax: +68 311 6689732.

E-mail addresses: habibi@chem.ui.ac.ir, habibi@sci.ui.ac.ir (M.H. Habibi).

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by a variety of methods such as polarography, conductometry, UV–visible, NMR, light scattering and electrolyte effect measurements [5,9]. Among these methods, the absorption UV–visible spectroscopy is one of the most suitable methods for quantitatively studying the aggregation properties of dyes as a function of concentration [7]. On the other hand, in spite of above mentioned spread applications of azo dyes, they are known to be largely non-biodegradable in aerobic conditions and to be reduced to more hazardous and carcinogenic intermediates in anaerobic conditions. Hence, the removing of these colorants from wastewaters has been attractive subject in the past decade years. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove color from textile effluents [18]. One of the new methods of treatment of wastewater containing dyes is their photocatalytic degradation in solutions illuminated with UV irradiation which contains a suitable photocatalyst, mainly TiO_2 or another one. This method was successfully applied to the decomposition of numerous organic substances, including azo and anthraqinonic dyes [19–22]. In order to achieve more effective photocatalytic degradation, it is necessary to consider the photophysico-chemical behavior of dye molecules. To the best of our knowledge, less attention has been paid to the effects of dye solution phenomena such as tautomerization, geometric isomerization, and/or dye molecules aggregations on the photocatalytic degradation of polyazo dyes. Only a few data in relation with tautomerization effect on the photooxidation of a mono-azo Acid Orange 7 (AO7) and in relation with photodegradation and trans–cis photoisomerization of Carotenoids on the CdS and ZnO have recently been reported [23–25] but for polyazo dyes, so far, no data have been reported. Therefore, in continuation of our ongoing program to develop photocatalytic reactions, we wish to report the dye aggregation and tautomerism effects on the photocatalytic degradation of Solophenyl red 3BL (C.I. Direct 80) polyazo dye in aqueous TiO_2 suspension.

2. Experimental

2.1. Material

Chemical structure of Solophenyl red 3BL (C.I. Direct 80) polyazo dye (shown in Scheme 1) obtained from the Ciba-Geigy was used as received without further purifications. KBr, KOH and H_2SO_4 were obtained from Merck. The pH value of solutions was adjusted with H_2SO_4 and KOH solutions and water for dye solution preparation was doubly distilled. The commercially available TiO_2 powder is mostly anatase in crystalline form with a surface area of about 50 m^2/g and primary particle size of 30 nm, the photocatalytic activity of this catalyst was much higher than TiO_2 rutile, was obtained from Merck.

2.2. Absorption measurements

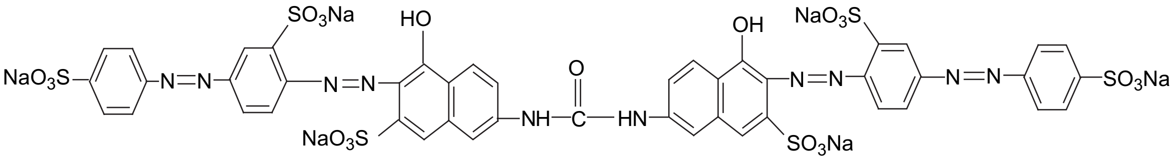
A double beam Varian Cary 500 Scan UV–visible spectrophotometer was used to record absorption spectra over a wavelength range 200–800 nm which combined with a cell temperature controller with accuracy of ±0.1 °C. Quartz cuvettes were used for measurements in solution via $l = 1$ cm.

2.3. Infrared spectroscopy

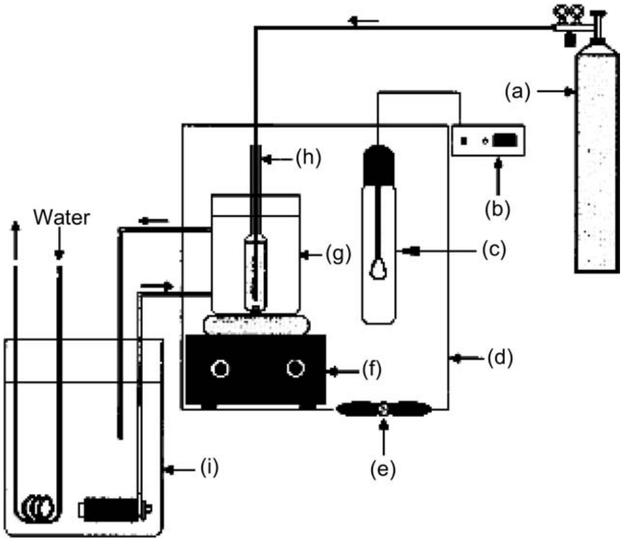
Infrared (IR) spectroscopy measurements were performed using a Shimadzu spectrophotometer in transmittance mode and IR spectra were taken in KBr discs at the range 400–4000 cm^{-1}.

2.4. Apparatus and procedures of photocatalytic degradation

Photocatalytic degradation process was carried out in a photodegradation cell of 200 ml in volume with a high-pressure mercury lamp of 400 W as shown in Scheme 2. Fresh dye solutions were prepared before use and diluted according to the requirements of the experiments and adjusted to known pH and allowed to stand for 30 min. The photodegradation cell was fed with 50 ml of the solution with stirring. During irradiation, agitation was maintained to keep the suspension homogenous. Samples ca. 2 ml were withdrawn for UV–visible analysis and centrifuged for 20 min at the rate 2000 rpm. The temperature of the process was maintained at 25 ± 0.1 °C by water circulation and TiO_2 photocatalyst amount during the whole experiments was 1 g/l.



Scheme 1. Chemical structure of commercial Solophenyl red 3BL (C.I. Direct 80) polyazo dye.



Scheme 2. Photodegradation set up for polyazo dye: (a) oxygen cylinder; (b) power supply; (c) 400 W high-pressure mercury lamp; (d) photoreactor with aluminium foil as reflector for a full irradiate of catalyst; (e) fan; (f) magnet stirrer; (g) 2 liter Pyrex beaker; (h) photodegradation cell; and (i) water thermostat Haake model F-122.

3. Results and discussion

3.1. Effect of concentration

Fig. 1 shows the electronic absorption spectra of Solophenyl red 3BL in aqueous solution with various dye concentrations (pH = 7.32). The UV–visible spectrum of 3BL dye consists of many absorption bands. It is observed that the absorption spectrum of 3BL is characterized by two bands in the visible region, with their maxima located at ca. 570 and ca. 380 nm, and by two bands in the ultraviolet region located at ca. 230 and ca. 280 nm (trace b). The absorbance bands at 230 and 280 nm are due to the benzene and naphthalene rings of 3BL, respectively, and are assigned to a $\pi \rightarrow \pi^*$ transition. The two bands in the visible region are due to the chromophore-containing azo linkage. It seems that the less intense band centered at ca. 380 nm is due to the partly forbidden $n \rightarrow \pi^*$ transition. On the other hand, the more intense broad band is attributed to the presence of two forms of the dye molecules (viz. azo at ca. 520 nm and hydrazone tautomers at ca. 570 nm) in solution and stems from an allowed $\pi \rightarrow \pi^*$ transition. 3BL is subjected to intramolecular hydrogen bonding tautomeric interactions between the hydrogen of hydroxyl group on the naphthyl group and the corresponding azo linkage. The hydrazone form is bathochromic compared to the azo form and has usually a higher tinctorial strength. Therefore, the band at higher wavelength corresponds to the hydrazone form, whereas the band at lower wavelength is linked to the azo form of 3BL dye. The shape analysis of this broad band at ca. 570 nm shows that the ratio of azo form to the hydrazone form in aqueous solutions is much higher because the azo form is favored by water due to intramolecular hydrogen bonding. Furthermore, by increasing dye concentration from 4×10^{-6} to 4×10^{-4} mol dm^{-3} (b–d), a new band in relation to aggregation of dye molecules was not observed and only the intensity of characteristic bands was increased. Therefore, it seems that this polyazo dye remained mostly in non-aggregated form by concentration variation in neutral aqueous solution. It should be noted that the higher concentrations of 3BL dye (4×10^{-3} mol dm^{-3}) was not detected by our spectrophotometer with quartz cuvettes via $l = 1$ cm as shown in the inset of Fig. 1 (case a).

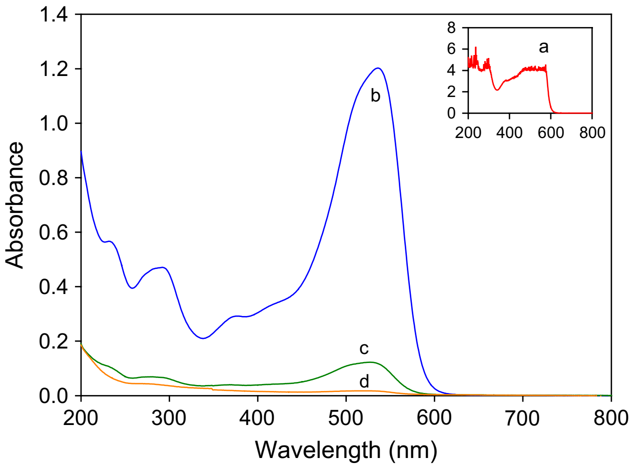


Fig. 1. UV–visible absorption spectra of Solophenyl red 3BL in aqueous solution at different dye concentrations. (a) 4×10^{-3}, (b) 4×10^{-4}, (c) 4×10^{-5} and (d) 4×10^{-6} mol dm^{-3}.

3.2. Effect of pH

Fig. 2 shows the absorption spectra of Solophenyl red 3BL (4×10^{-5} mol dm^{-3}) in aqueous solution at different pH. The results showed that for the freshly prepared aqueous 3BL dye solution in pH range from 1.14 to 11.9, the pH variation did not influence the UV–visible absorption spectra which means that the aggregation did not occur. At this stage the colors of three solutions (low acidic, neutral and basic) were red.

3.3. Effect of time

Three solutions of the former stage were allowed to stand for ca. 10 h and the color of Solophenyl red 3BL (4×10^{-5} mol dm^{-3}) in aqueous solution at pH less than 1.14 changed to blue (case (a) as inset of Fig. 3). This is due to a new feature formation in this solution pH, while the color of other solutions did not change in the elapsed time (cases (e) and (f) in Fig. 3). As shown in Fig. 3(a), a new J-aggregate dimer is observed in the acidic aqueous solution which has

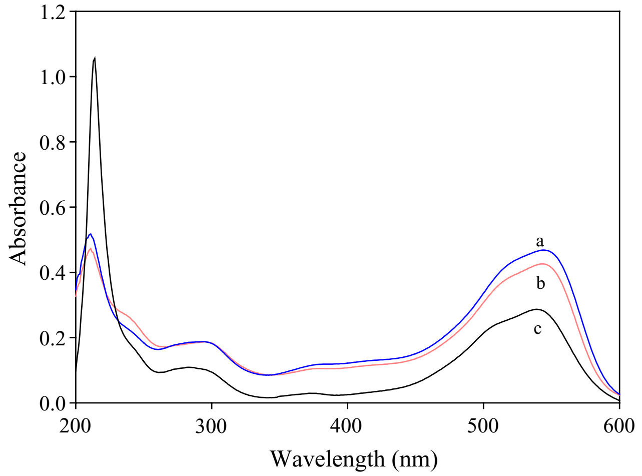


Fig. 2. Absorption spectra of freshly prepared Solophenyl red 3BL aqueous solution at different pH. (a) 1.14, (b) 7.32, and (c) 11.90.

a red shift with respect to that of monomer molecules in cases (d–f) in Fig. 3. The results showed that the variation of solution pH from cases (a) to (d) causes the disappearance of aggregation.

3.4. Reproducibility of aggregation

Experiments showed that Solophenyl red 3BL molecules possess aggregation in acidic aqueous solution at longer times. By decreasing the solution pH, dye molecule aggregation occurred at reduced time. In highly acidic solutions (pH = 0.2) both monomer and dimer molecules exist (case (b) in Fig. 4). By dilution of solution (b) aggregated feature disappeared completely (cases (c) and (d)). But at pH ⋘ 0.2 only dimmer molecule was observed (case (a) in Fig. 4). By increasing the solution pH, aggregated feature disappeared completely (cases (e) and (f)).

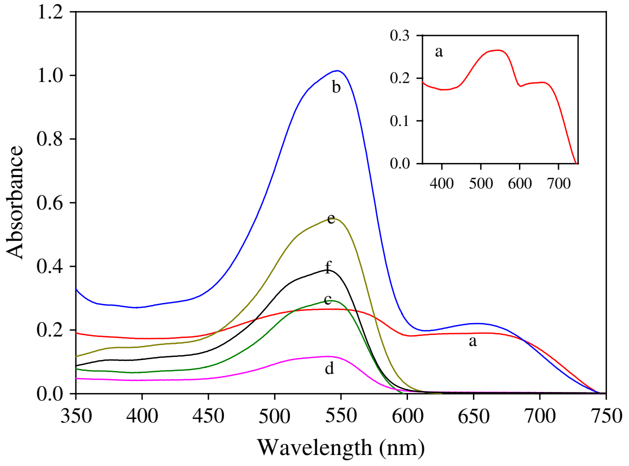


Fig. 3. Absorption spectra of aggregated Solophenyl red 3BL aqueous solution (4×10^{-5} mol dm^{-3}) at different pH after 10 h. (a) Less than 1.14, (b) 1.14, (c) 3.00, (d) 4.20, (e) 7.32, and (f) 11.90.

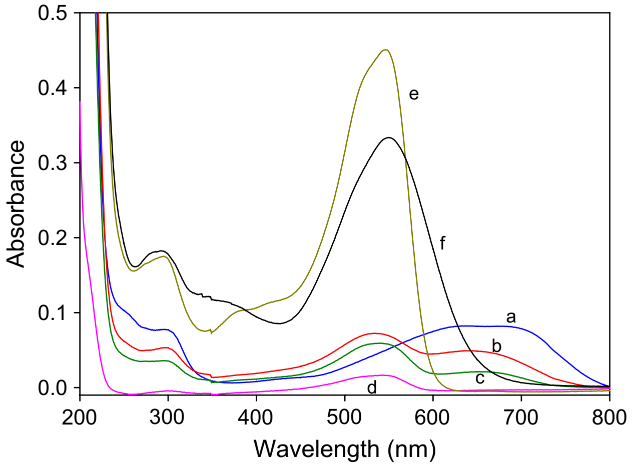


Fig. 4. Absorption spectra of aggregated Solophenyl red 3BL aqueous solution at different solution pH. (a) Less than 0.20, (b) 0.20, (c) 0.63, (d) 2.00, (e) 7.00, and (f) 10.03.

3.5. Infrared spectroscopic studies

Fig. 5 shows the infrared spectra of 3BL dye in aqueous solution at various solution pH (a, 7.32; b, 11.90; and c, 1.14). As shown in this figure, in neutral and basic solutions cases (a) and (b), the IR spectra are very similar and carbonyl functional group stretch bands are observed at about 1750 cm^{-1}. While in high acidic solutions, case (c), carbonyl functional group stretching band is omitted and OH group stretching band is appeared at about 3000 cm^{-1}. Therefore, it seems that the carbonyl functional group of Solophenyl red 3BL in highly acidic aqueous solution aids to form J-aggregate feature. The color of dye in the neutral and basic solutions was pinkish red while in the highly acidic solution it was changed to blue.

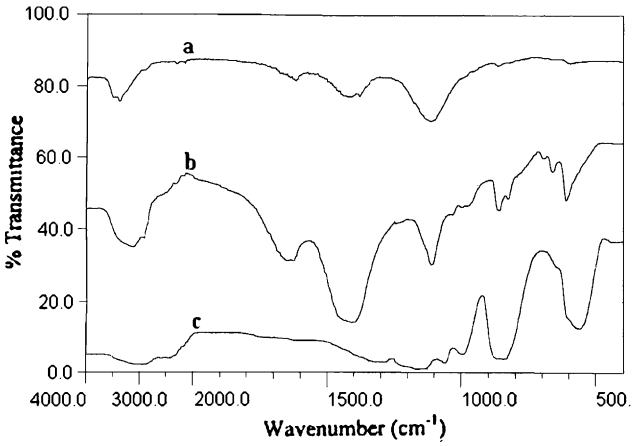


Fig. 5. Infrared spectra of 3BL dye in aqueous solution at various pH. (a) 7.32, (b) 11.90, and (c) 1.14.

3.6. Photocatalytic degradation of 3BL dye in aqueous solutions

In order to observe the effect of aggregation and azo–hydrazone tautomerism on the photocatalytic degradation of 3BL dye (5×10^{-5} mol dm^{-3}) in aqueous solution, experiments were carried out by varying the solution pH. Before photocatalytic degradation, the UV–visible absorption spectra of 3BL dye were taken and are shown in Fig. 6. As shown in this figure, in highly acidic aqueous solution there is only one absorption band which is centered ca. 650 nm, whereas in the Figs. 3 and 4 a plateau appeared in this wavelength region. Discrepancy can be explained by the level of solution pH. In the latter cases the solution pH was extremely low but in the former case the level of solution pH is relatively high, hence in the latter cases both of the aggregated dimers exist in the aqueous solution with equivalent probabilities, but in the former case by decreasing solution pH, the contributions of two aggregate features were varied. In comparison with Figs. 3 and 4, it is clear that a similar trend is observed in Fig. 6. For instance, in curve (b) we observed both monomer and dimer features. On the other hand, as we expected in the neutral and basic aqueous solutions only monomer appeared. We used these solutions for photocatalytic degradation purposes in the next stages.

3.7. Photocatalytic degradation of 3BL dye in high acidic solution

The obtained results of 3BL dye photocatalytic degradation in high acidic aqueous solution are shown in Fig. 7. As it can be seen before photocatalytic degradation, dye molecules exist in J-aggregate form (case a). But after 15 min UV-light irradiation over TiO_2 surface the most of dye molecules were degraded. However, it is clear that the great percent of molecules still exist in J-aggregate form. After 45 min UV irradiation no significant progress was observed in the photocatalytic degradation of dye solution. Since the pH of zero charge point of TiO_2 is ca. 7, therefore under this pH value the surface charge of TiO_2 is positive and anionic dyes can be easily adsorbed on the TiO_2 surface. But in the extremely acidic aqueous solution, 3BL dye molecules were aggregated with no charge. Therefore, as we expected after a long elapsed time complete degradation could not be observed.

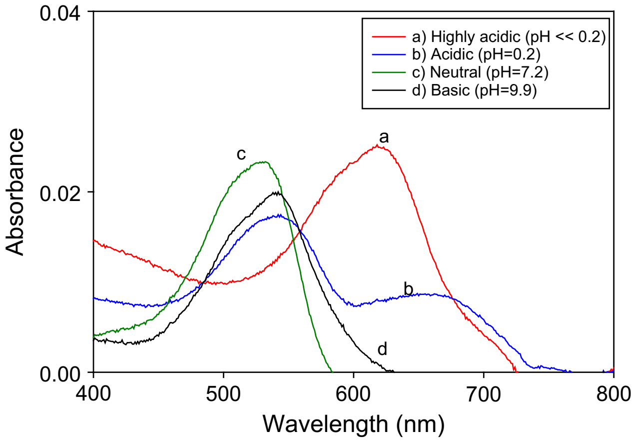


Fig. 6. UV–visible absorption spectra of Solophenyl red 3BL in aqueous solution at different solution pH before photocatalytic degradation under UV irradiation. (a) Less than 0.20, (b) 0.20, (c) 7.20, and (d) 9.90.

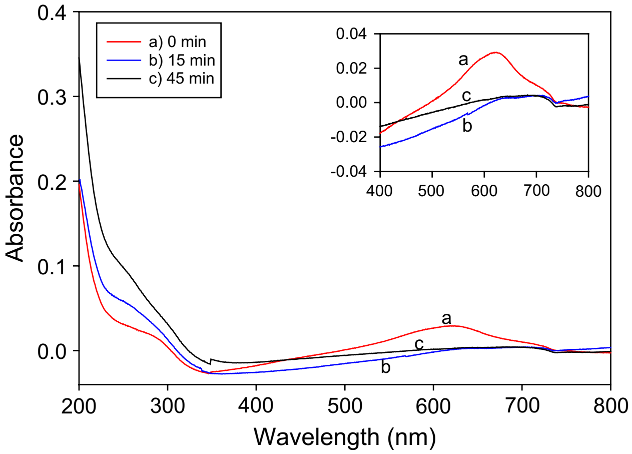


Fig. 7. UV–visible absorption spectra of Solophenyl red 3BL in high acidic aqueous solution (pH $\ll$ 0.20) after photocatalytic degradation under UV light irradiation on TiO_2 surface.

3.8. Photocatalytic degradation of 3BL dye in acidic solution

Photocatalytic degradation of 3BL dye in acidic aqueous solution is shown in Fig. 8. It is clear that before photocatalytic degradation, dye molecules exist in both aggregated and disaggregated form (case a). But after 15 min of UV irradiation most of the dye molecules have been degraded. Further UV irradiation did not have any significant effect on the photocatalytic degradations.

3.9. Photocatalytic degradation of neutral 3BL dye solution

Photocatalytic degradation of 3BL dye in neutral aqueous solution is shown in Fig. 9. Before the photocatalytic degradation, dye molecules exist in disaggregated form (case a), but after 15 min of UV irradiation the most of dye molecules were degraded and

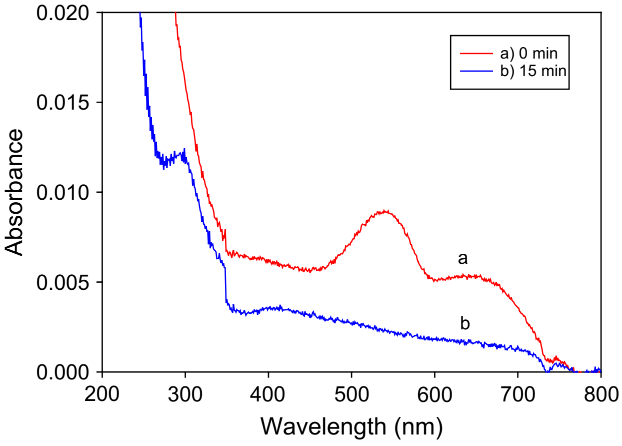


Fig. 8. UV–visible absorption spectra of Solophenyl red 3BL in acidic aqueous solution (pH = 0.20). (a) Before and (b) after photocatalytic degradation under UV light irradiation on TiO_2 surface.

further UV irradiation did not have any significant effect on the dye molecule degradations.

3.10. Photocatalytic degradation of basic 3BL dye solution

Photocatalytic degradation of 3BL dye in basic aqueous solution is shown in Fig. 10. Before photocatalytic degradation dye molecules exist in disaggregated form (case a). But after 15 min UV light irradiation, the whole dye molecules were degraded and further UV irradiation did not have any significant effect on the dye molecule degradations. It is worth to note that in the basic aqueous 3BL dye solutions complete degradation of dye molecules and complete mineralization were impossible because of anionic dye molecules and anionic TiO_2 surface columbic repulsions.

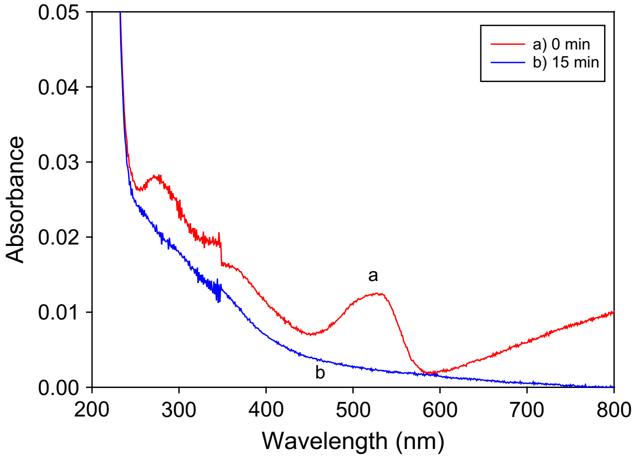


Fig. 9. UV–visible absorption spectra of Solophenyl red 3BL in neutral aqueous solution (pH = 7.20). (a) Before and (b) after photocatalytic degradation under UV light irradiation on TiO_2 surface.

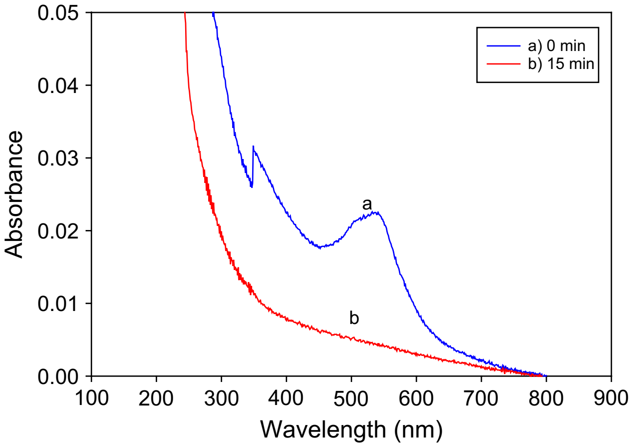


Fig. 10. UV–visible absorption spectra of Solophenyl red 3BL in basic aqueous solution (pH = 9.90). (a) Before and (b) after photocatalytic degradation under UV light irradiation on TiO_2 surface.

3.11. Comparison of photocatalytic degradation of 3BL dye at different pH

In order to better understand the influence of dye molecule aggregation on photocatalytic degradation in aqueous solutions, the degradation results of all 3BL dye solutions at different pH after 15 min were compared and are shown in Fig. 11. The best photocatalytic degradation was observed for acidic 3BL dye solutions, while for high acidic 3BL dye solution some residual absorption due to dye molecule aggregation was observed which prevented further photocatalytic degradation. Of course, we know that the extremely acidic solution has strong effect on the photocatalyst. Because in this solution pH, water molecules could be adsorbed on the photocatalyst surface and/or bisulfate (or sulfate) ions could also be strongly adsorbed on the photocatalyst surface which

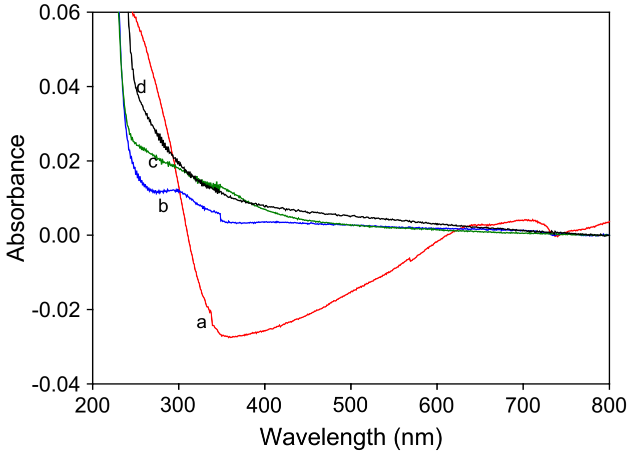


Fig. 11. Comparison of UV–visible absorption spectra of Solophenyl red 3BL in different aqueous solution pH after photocatalytic degradation under UV irradiation. (a) Less than 0.20, (b) 0.20, (c) 7.20, and (d) 9.90.

probably prevented the progress of the photodegradation. In addition, a negative absorbance value in the highly acidic solution was observed which can be explained by the solution reflective index changes upon photodegradation of dye molecules.

4. Conclusion

From our findings the following conclusions can be drawn:

- UV–visible spectroscopy studies show that in the aqueous neutral solution, the increasing of dye concentration do not form dye molecule aggregation.
- Just only in acidic aqueous solutions a J-aggregate 3BL dye molecule formation is possible. By increasing the solution acidity (i.e. lower pH) the probability of aggregation is increased.
- In the relatively acidic solution, aggregation of dye molecules was time dependent.
- Infrared spectroscopic studies further confirmed the aggregation of 3BL dye molecules in highly acidic aqueous solutions.
- Since, in the extremely acidic aqueous solution 3BL dye molecules was aggregated therefore complete photocatalytic degradation after a long elapsed time is not achieved, but in the low acidic aqueous solutions better degradation is observed.
- The obtained results showed that the azo–hydrazone tautomerism has no significant effect on the photocatalytic degradation of Solophenyl red 3BL in all aqueous solutions.

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