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Dye–micelle aggregate formation for effective photobleaching

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Abstract

Incorporation of six different (three cationic: MB, CV, AO and three anionic: RB, E and Fl) dye molecules in three different micellar environments has been examined critically for photobleaching of the dye–micelle aggregates. Micellar media have been found to influence the rate of decolorization which has been explained considering electrostatic, hydrophobic and charge transfer interactions. Further rate enhancement of colour bleaching was observed with Se nanoparticles. In depth, kinetic studies have been carried out to realize the interaction of the dyes with micelles. Kinetic studies have revealed that the reaction is first order with respect to dye concentration.

Keywords: Micelle; Dye; Degradation; Colour; UV light; Kinetics

1. Introduction

Photochemical systems for photoreduction of water are of considerable interest as models for the conversion of solar energy. In so-called sacrificial systems, hydrogen ions are reduced by electrons which are derived from the added donor rather than from the oxidation of hydroxyl ions [1–3]. Compared with metal complexes, organic dyes have been investigated only rarely as sensitizers for the photoreduction of water [4–6]; however, because of the common availability of organic dyes, it is of interest to explore the potential of representative examples as sensitizers. Dyes have also been found as an important component in initiator systems for photopolymerization induced by polychromatic light [7–9]. Relevant photoinitiator compositions often contain two different initiator systems, one absorbing visible light (dye system) and the other being sensitive only to UV light. In typical dye systems, a co-initiator is needed for the formation of species capable of initiating the polymerization. Such systems, which function on the basis of the photoreduction of dyes, are well-known [10]. Amines are quite appropriate as reductants because of their favorable and easily variable oxidation potentials [9]. Textile dyes and other commercial colorants have become a major concern to environmental pollution. Many dyes are made highly water-soluble in order to meet the colour requirement of deep dyeing. As a consequence traditionally wastewater becomes contaminated and treatment methods such as flocculation, activated carbon adsorption and biological treatment are becoming increasingly ineffective. There are reports where dye degradation has been done photochemically, using semiconductor materials such as heterogeneous catalysts [11–14], Fenton's reagent [15], cyclic ketones [16] etc. Aqueous micellar solution has the ability to solubilize different kinds of organic

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molecules and to catalyze a wide variety of reactions. Reduction of same dye under different micellar environment and using different reagents can take place following different mechanisms [17–19]. The micelles are well-known membrane mimetic system [20–22] and it is known to function in many ways. Micelles enhance the solubility of organic compounds in water [23] owing to their incorporation in the micelle [24], catalyze many reactions due to the 'concentration effect' in the micellar pseudo-phase [25] and also alter the reaction pathways [26] in many cases. Thus solubilization of a dye in a micelle and thereby the photoactivation of dye–micelle aggregates might serve a variety of purposes [27]. Depending on the nature of the head group, micellar surface can be cationic, anionic and non-ionic. Such organized media might offer electrostatic, hydrophobic and charge transfer interactions with the incoming species. It has been found that the strong electrostatic interaction plays a deterministic role to change the rate of reaction as well as the reaction pathway. Recently, our group has shown such type of electrostatic interaction in organized media [28]. There has been similar report also on dye–micelle interaction, where electrostatic interaction plays a leading role in the reaction [29]. In some cases [17], not charge compensation but the hydrophobic interaction, becomes predominant in the reaction condition. Again, Bunton and co-workers [30] have shown that dyes with sulphonic acid functionalities are incorporated in the Stern layer of cationic micelle in a sandwich arrangement and suggested a van der Waals type interaction between adjacent surfactant chains and the organic dye moieties. The effect of micelles can be physically interpreted by the decrease in the degree of freedom of the reactants in solution. The binding of at least one of the reactants facilitates any other diffusing reactant to approach towards a fixed target. This physical factor has been rationalized as an explanation of the increase in rate of the reaction in the micellar medium.

Herein, we report the photodegradation of a few well-known cationic and anionic dyes by UV light that too in micellar environments. The effect of different micro-environment on the absorption characteristics of the dye and their rate of degradation has been studied in depth using three anionic and three cationic dye molecules with different skeletons after incorporating them in different micellar environments. Dyes and micelles remain alive for long in surface aquatic reserves and hence the dyes and micelles in this work were selected for degradation of the dyes upon the absorption of light over a wide range of the visible spectrum. Again, the photobleaching has been found to be exalted with Se nanoparticles. These dyes are well-known as sensitizers in photography, redox indicator in chemistry and most recently, active media for use in dye lasers and sensitizers for the formation of singlet oxygen.

2. Experimental details

2.1. Materials

The dyes Methylene Blue (S. D. Fine Chemicals, India), Crystal Violet (Aldrich), Acridine Orange (Merck), Rose Bengal (S. D. Fine Chemicals, India), Eosin (Merck) and Fluorescein (Merck) were used as received. Cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were purchased from Aldrich and purified by repeated crystallization from acetone. Poly(oxyethylene)-*iso*-octyl phenyl ether, TX-100 (Aldrich) was used as received. Double distilled water was used throughout the whole experiment.

2.2. Spectroscopic measurements and techniques

Aqueous stock (10^{-2} M) solutions of dyes were prepared. Three different surfactant solutions (10^{-2} M) (SDS, CTAB and TX-100) were prepared using double distilled water. Aliquots (3 mL) of each dye solutions were taken in stoppered quartz cuvettes and exposed to UV irradiation individually in a photoreactor. Separate photoirradiations were carried out in a photoreactor fitted with ordinary germicidal lamps capable of emitting light of wavelength ~ 365 nm (Philips, India). The photoreactor can produce a flux of 850 lux (1 lux means 1 lumen flux of photon per square centimeter per second). The flux was monitored using a digital lux meter (Model LX-101), Taiwan. The photoreactor (intensity of light) was calibrated with an Ophir power meter (NOVA display and 30-A-SH sensor). The number of photons absorbed per unit area of the sample per second from the photoreactor of 100 lux is 3.03×10^{15}. All UV–visible absorption spectra were recorded in a Shimadzu (Kyoto, Japan) UV-160 digital spectrophotometer equipped with 1 cm quartz cells.

3. Results and discussion

3.1. Absorption characteristics of different dyes in different micellar media

For comparative analysis a series of dyes and a series of surfactants were selected. The dyes include both cationic and anionic types. The selected cationic dyes were Methylene Blue (MB), Aciridine Orange (AO), and Crystal Violet (CV) and the anionic dyes were Rose Bengal (RB), Eosin (E) and Fluorescein (Fl). Three different types of surfactants were used: Triton X-100 (TX-100) as non-ionic, sodium dodecyl sulfate (SDS) as anionic and cetyltrimethyl ammonium bromide (CTAB) as cationic. To make a comparative study, the dye bleaching was carried out in water also. The structures of different dyes and their absorption maxima in different micellar environment are shown in Table 1. It has been noticed that there is a significant blue shift in the λ_{max} values in case of CV in SDS micelle indicating a strong ionic interaction [18]. The same is true for RB when it is housed in CTAB medium. On the other hand, a sufficient red shift in case of RB, E and FL in TX-100 medium indicates dye aggregation (as J or H aggregate), which has been reported already [31]. It has been reported that the formation of dye–dye, aggregate (J or H aggregate) is a very difficult proposition, but under the forced condition where no other interaction is possible the dye–dye interaction might take place. Possible dye aggregates were not evidenced between SDS and the anionic dyes presumably due to the electrostatic repulsion.

3.2. Photobleaching of dye–micelle aggregates under UV illumination (>254 nm)

The absorption spectra of the dye RB and CV in TX-100 and their color bleaching with time have been shown in Fig. 1. The dye RB and CV in TX-100 showed λ_{max} at 562 nm and 598 nm, respectively. The absorption spectrum after UV irradiation was recorded using the UV–visible spectrophotometer. The surfactant concentrations in all cases were in the range of 10^{-2}–10^{-1} M i.e., above the critical micellar concentration (CMC). It was observed that the change of surfactant concentration from 10^{-2} to 10^{-1} M did not cause any noticeable change in the rate for photobleaching. When the concentrations of the surfactants are very close to their CMC values, the visible spectra of the dyes red shifted as more dye molecules are taken into the micelles. When the concentrations of the surfactants are well above their CMC, the values of λ_{max} became nearly constant; this is caused by the solubilization of large amount of dye into the micelles. Table 2 shows the characteristic (the number of light and their relation with the lux and photon/cm^2) of the photoreactor. The dye degradation was studied under variable light intensities by controlling the illumination during the photodegradation and it was observed that the rate becomes faster with higher light intensities i.e., with higher flux. It was also noticed that when the reaction was carried out in the absence of O_2 it did not affect the rate of color bleaching. Also once the bleaching is complete the colour of the dye never reappeared even by bubbling air for at least ½ h. No photobleaching was observed while the reaction was carried out in glass cell in lieu of quartz cell. Sunlight also could not bring about the photobleaching reaction while the dye solutions were exposed to solar irradiation for ~2 h.

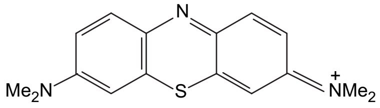
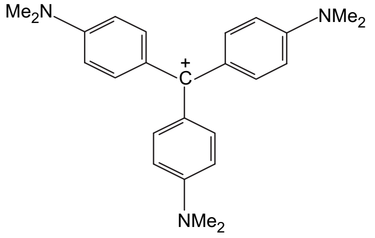
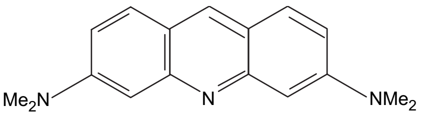
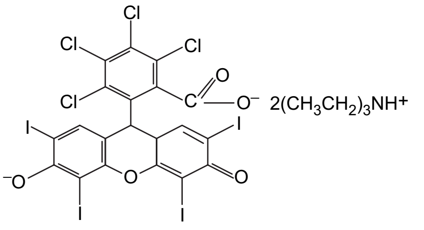
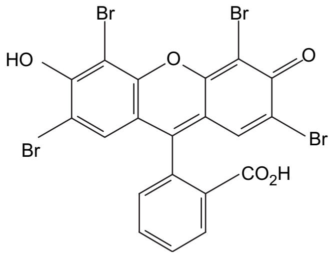
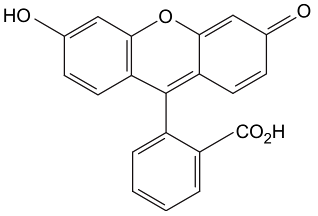
3.3. Kinetic studies on dye bleaching under various micellar environments

Kinetics of dye degradation was studied for all the dyes in presence of three types of micelles and in aqueous environment. The surfactant concentration was maintained at 10^{-2} M in all the cases. The time dependent bleaching of the dyes for all the cases is shown in Fig. 2a–f. In all cases, they followed first order kinetics. The first order rate constant for all the systems are given in Table 3. It is observed that in case of cationic dyes the rate is highest in TX-100 while compared to other micellar environment or in aqueous solutions. The rate of photobleaching for cationic dyes follows the order

$$\text{Rate}_{\text{TX-100}} > \text{Rate}_{\text{SDS}} > \text{Rate}_{\text{CTAB}} > \text{Rate}_{\text{H}_2\text{O}}.$$

In all the cases, the reaction is very slow in aqueous medium. In micellar medium two different types of interactions are possible with the dyes in question depending on the nature of micelle and dye. One is the ionic interaction, which may be either attraction (between two opposite kinds of charges) or repulsion (between two similar kinds of charges). The other is the hydrophobic interaction occurring thorough the long-chain hydrocarbon moiety. Both types of interaction can take a predominant role and cause increase/decrease in the reaction rates [17–19] depending on the type of reaction and the substrates taking part in the photophysical process. Previous reports showed that hydrophobic interaction plays the deterministic role in dye–surfactant interaction [17,18], although the exact nature of this interaction in many cases has not been satisfactorily explained. In our study, non-ionic micelle takes the leading role and shows the dominant effect for interaction with a cationic dye when rates are concerned indicating that it is the hydrophobic interaction between cationic dye and TX-100 micelle which is responsible for the rate enhancement. However, in case of TX-100 micelle there is charge transfer interaction between the cationic dye and the micelle where TX-100 acts as a donor and the dye being the acceptor [32]. The electron donor property of the TX-100 has also been confirmed by its charge transfer interaction with an electron acceptor like iodine [33]. It is quite reasonable why in simple aqueous medium and in cationic micelle the rates are very small in all cationic dye cases. This is because there is no "concentration effect" in the micellar pseudo-phase in case of CTAB micelle due to charge–charge repulsion. The increase in absorbance with increase in surfactant concentration is regarded to be caused by the dye molecule penetration into micelles, as observed for other additives. Although, the dye molecules are incorporated in the micelles, the chromophores of their molecules are still oriented near the surface like an antennae and absorb the light more favorably than in the

Table 1
Different dyes with λ_{max} values in aqueous and micellar medium

Dye	Structure	λ_{max} (nm)			
		H_2O	SDS	TX-100	CTAB
Methylene Blue (MB)		662	660	664	664
Crystal Violet (CV)		598	593–573	598	593
Acridine Orange (AO)		490	496–487	495	491
Rose Bengal (RB)		548	550–542	562–568	560–522
Eosin (E)		516	516	534	524–510
Fluorescein (Fl)		489	488	500	489

bulk aqueous solution. But in presence of CTAB, the spectrum for the cationic dyes is not perturbed at all, which is an indication that CTAB and the cationic dyes do not interact at all.

A complete different feature is noticed for the first time in case of anionic dyes in different micelles. It is very interesting to observe that all anionic dyes used for our studies showed a considerable ($\Delta\lambda \sim 18$ nm) red shift in

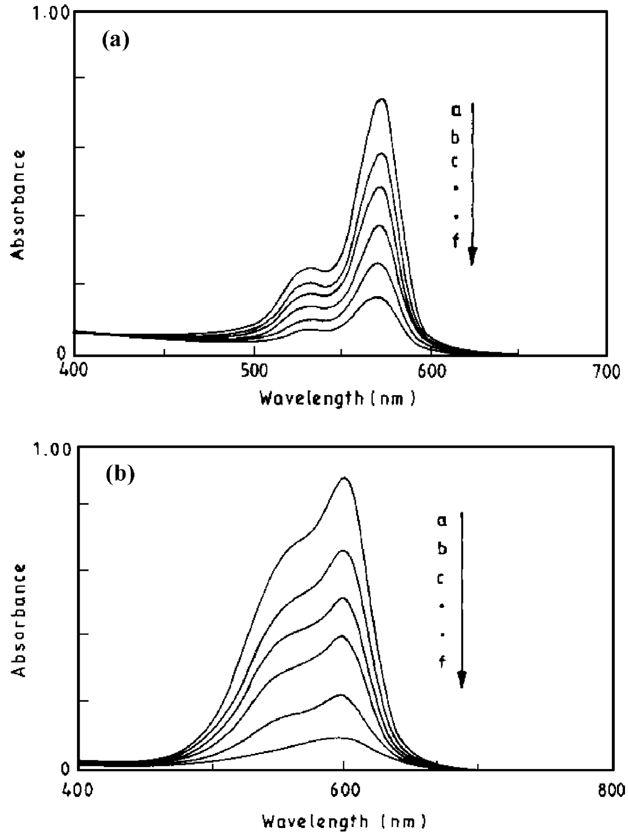


Fig. 1. UV–visible spectra for the photodecolorization of: (a) Rose Bengal and (b) Crystal Violet by UV light in TX-100 micellar medium. The time interval between successive measurements is 4 min. Condition: concentration of RB = 4.76×10^{-4} M, CV = 4.76×10^{-5} M, concentration of TX-100 = 9.5×10^{-3} M. Flux of UV light = 340 lux.

the λ_{max} in TX-100 micelle when compared to that in water. This is a clear indication of the formation of dye aggregate (J or H type) in presence of the non-ionic micelle. For the other two types of micelles there is no considerable λ_{max} shift when compared to that in water. Here the micelle (TX-100) offers this strained condition hence the dye aggregation is only possible in non-ionic micelles like TX-100. Dye–dye aggregation is most probable in TX-100 micellar surface because it is a neutral micelle and hence the other type of interaction (columbic) is not possible here, whereas, ionic interactions prevail in case of charged micelles. However, in the latter case the effect of ionic strength of the medium has been observed to be less important because of the insignificant number of counter-ions out of ionic surfactant molecules. Taking all the facts in consideration, it has been suggested that non-columbic interactions make a sizeable contribution to the free energy of binding between the cationic surfactant and the anionic dyes. The dye with a negative charge interacts with the positive head groups of CTAB. Therefore, the dye molecules remain most of the time at the outer surface of the micelles [34]. One observation is that CTAB head groups are tightly associated with the aromatic ring of the solubilizate [30] and consequently a dye molecule does not penetrate very deeply into CTAB micelles, unless the dye's hydrophobicity is high enough to overcome this interaction. Moreover, simple ion-pairing between a negative group such as $-SO_3H$, or $-COOH$ of the dye and a quaternary ammonium ion does not perturb the chromophore. In the presence of cationic surfactants, aromatic compounds with "sulphonic or carboxylic acid groups" do not act simply as counter-ions, but are incorporated into the water-rich Stern layer of the micelle in a sandwich arrangement. This permits not only the hydration of the hydrophilic $-SO_3H$ (or $-COOH$) group, but also the solvation of the aromatic ring of the dye and the participation of van der Waals interactions between adjacent surfactant chains and the dye organic moiety (hydrophobic forces). In this situation, the micro-environment of the chromophore has clearly changed, from that existing in the bulk aqueous phase, and this change is the cause of the spectral shifts observed. The red shift depends on the nature of charge present on the surfactant head group. Electric transition energy is inversely proportional to the $\Delta\lambda_{max}$. Here in the case of TX-100 there is strong interaction between the dye and the micelle as TX-100 is bulkiest among the three micelles used. Therefore, the electrical transition energy is less in case of TX-100 as here interaction is not so strong. So a large value for $\Delta\lambda_{max}$ was found here. On the other hand for the anionic surfactants there is strong repulsion between the dye molecule and the anionic head group of the surfactant.

Table 2
Characteristic photon emission from the photoreactor

Number of UV tube used	Flux (Lux)	Approximate number of photon adsorbed per unit volume of the sample per second from the photoreactor
1	100	3.03×10^{15}
2	220	6.66×10^{15}
3	340	1.03×10^{16}
4	470	1.42×10^{15}
5	600	1.818×10^{16}
6	740	2.24×10^{16}
7	900	2.727×10^{16}
8	1040	3.151×10^{16}

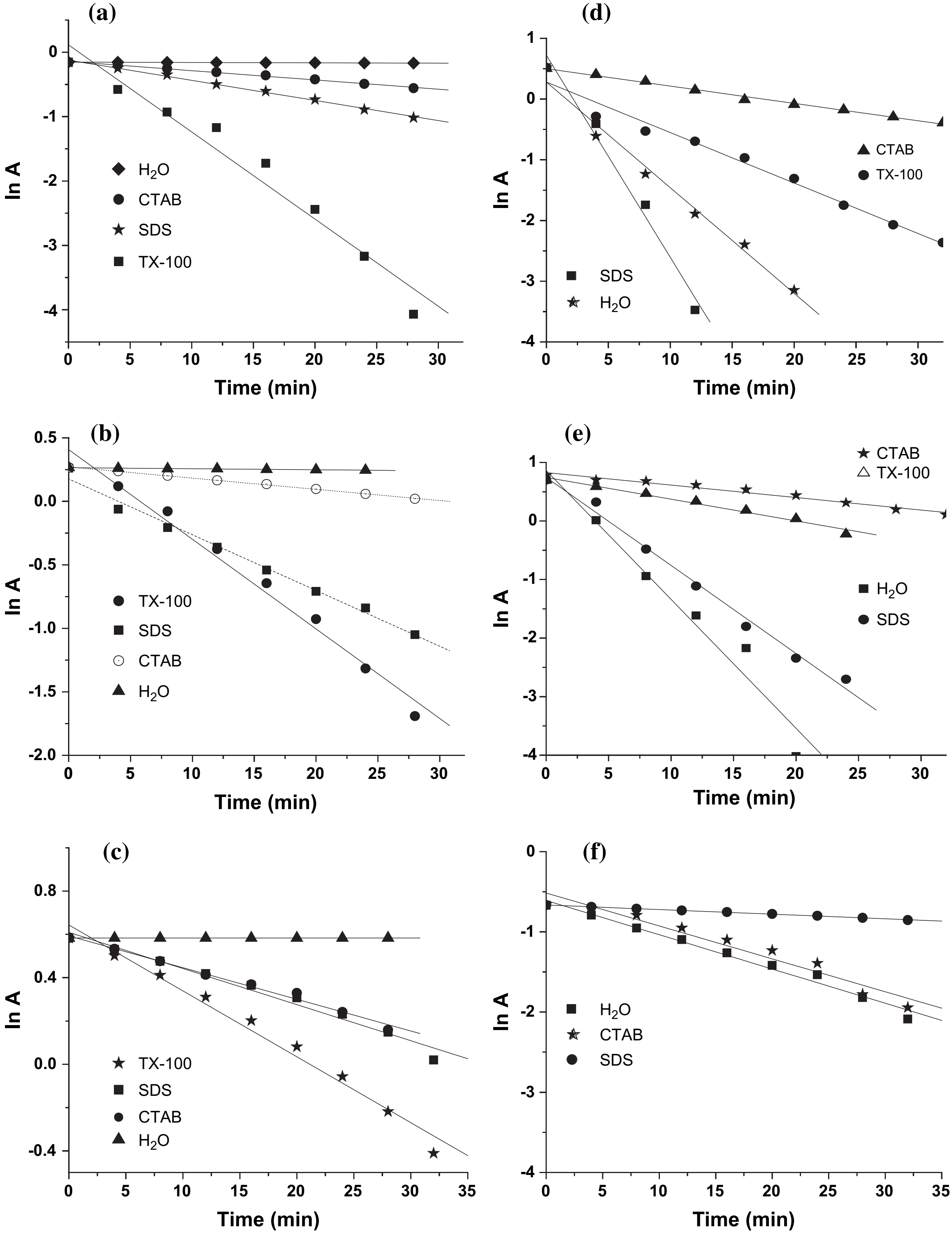


Fig. 2. Plot of $-\ln A_t$ vs. time of the photodecolorization of: (a) Methylene Blue, (b) Crystal Violet, (c) Acridine Orange, (d) Rose Bengal, (e) Eosin, and (f) Fluorescein in water, CTAB, SDS and TX-100 micellar medium. Condition: $[\mathrm{MB}] = 2.4 \times 10^{-5}$ M, $[\mathrm{CV}] = 4.76 \times 10^{-5}$ M, $[\mathrm{AO}] = 2.3 \times 10^{-4}$ M, $[\mathrm{RB}] = 4.76 \times 10^{-4}$ M, $[\mathrm{E}] = 4.76 \times 10^{-5}$ M and $[\mathrm{Fl}] = 4.76 \times 10^{-5}$ M. $[\mathrm{Micelle}] = 9.5 \times 10^{-3}$ M, flux of UV light = 340 lux.

Table 3
The first order rate constant values in water and in different micellar media

Dye	First order rate constant (min^{-1})			
	H_2O	SDS	TX-100	CTAB
Methylene Blue (MB)	0.535×10^{-3}	3.124×10^{-2}	13.53×10^{-2}	1.439×10^{-2}
Crystal Violet (CV)	0.817×10^{-4}	4.389×10^{-2}	7.055×10^{-2}	0.882×10^{-2}
Acridine Orange (AO)	–	1.668×10^{-2}	3.043×10^{-2}	1.46×10^{-2}
Rose Bengal (RB)	33.39×10^{-2}	17.27×10^{-2}	8.311×10^{-2}	2.85×10^{-2}
Eosin (E)	22.01×10^{-2}	15.05×10^{-2}	8.311×10^{-2}	2.85×10^{-2}
Fluorescein (Fl)	4.42×10^{-2}	4.10×10^{-2}	–	4.27×10^{-2}

But for the non-ionic surfactants there is no such interaction. Here the hydrophobic interaction plays the crucial role.

Looking into the structures of the anionic dyes it is assumed that hydrophobic interaction is very difficult to conceive because of steric factor. It is noticed that the rates of photobleaching for all the anionic dyes in water is quite significant and effective in comparison to the reaction in CTAB micelle, where ionic interaction prevails. All the anionic dyes bleached very slowly in TX-100 micelle. This is presumably due to the fact that the dye aggregates are not susceptible to photobleaching or in other words they are resistant to photobleaching under the experimental condition. In case of Fl in TX-100 the rate could not be followed because of instantaneous and fast redox reaction. In case of anionic dyes, although there is no generalized sequence of rate of photobleaching in different media, it is clear that unlike the cationic dyes, simple aqueous solution serves a better dispersion medium than the micellar environment in most cases for their photobleaching. For the photobleaching of the dye in presence of the surfactants the dye–micelle aggregates become the main component for interacting with UV light. The photobleaching depends on the ability of the dye–micelle aggregate to harvest the UV light. In case of TX-100 micelle the micelle–dye aggregated species is not susceptible for the reduction, hence the reduction rate is slow. These aggregated species cannot scavenge the light and hence reduction process becomes slow. In the other two ionic micellar cases the aggregated species harvest the light and hence facilitates the reduction process.

3.4. Photobleaching as oxidation mineralization

The photobleaching of dyes in presence of semiconductors such as TiO_2 either in the presence or in absence of O_2 is well studied [35]. Their photobleaching in micellar environment is not studied much. It was reported that the photobleaching of dyes in presence of TiO_2 can lead to mostly two types of reaction: (i) reduction to a leuco form of the dye and (ii) oxidation leading to mineralization, depending on the absence/presence of O_2. In the present study the reaction was carried out under aerobic condition and the bleaching was reversible indicating that the process was oxidized only by O_2 which is present in the solution in dissolved state. After the bleaching, in no case the colour is recovered when O_2 is passed for $>1/2$ h.

3.5. Study using metal particles

The photobleaching have again been studied in the presence of selenium nanoparticles [36] as a test case. Here we have considered Se particles as they have shown to be very effective in many catalytic processes [37]. To have a comparison, we also examined the photobleaching of a representative dye, CV in CTAB micelle in presence of Se. The colour bleaching has been found to be faster in this case (Fig. 3) than the uncatalyzed reaction. Selenium nanoparticles because of their inherent hydrophobic surfaces are entrapped in the micellar core [26] which in turn extracts the dye molecule. Thereby both the reactants get an avenue to come in contact with the entrapped Se particles and thus an effective electron transfer takes place.

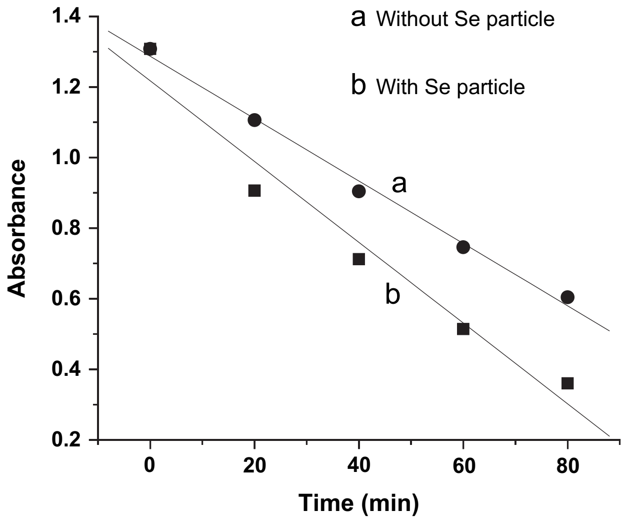


Fig. 3. Absorbance vs. time plot for the photodecolorization of CV: (a) in absence and (b) in the presence of Se particles. Condition: final concentration of CV in solution = 4.76×10^{-5} M; final concentration of the Se particles in the solution = 1.6×10^{-5} M, flux of UV light = 340 lux.

4. Conclusion

UV photoactivation technique has been employed for the decolorization of six different organic dyes in aqueous and micellar environment in a specified experimental time scale. The organized media provide geometric control of the reaction as well as the immobilization sites for the reactants. Thus, micelles provide a method of organizing the reaction on a molecular scale and enhance the rate of reaction. The study reports the catalytic activity of a restricted geometry and a typical environment of various organized assemblies. It was observed that the micellar catalysis is a consequence of three types of interactions: electrostatic, hydrophobic and charge transfer. The article reveals the attraction between cationic dye and neutral micellar system through charge transfer interaction where the TX-100 is the donor and the dye is the acceptor. On the other hand for anionic dyes again in TX-100, a strong steric interaction makes dye–dye aggregates that render the oxidation process slow. From the above study it can also be concluded that in case of cationic dyes the micellar environment has a meaningful effect for dye degradation but this is untrue for anionic dyes. Again, incorporation of Se nanoparticles has shown a profound influence in either cases of photobleaching. This study may thus be useful to degrade dye molecules in aqueous micellar environment and fabricating sensitized devices, dye lasers and photo devices taking stabilized dye aggregates into consideration.

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