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Photodegradation of dyes with poor solubility in an aqueous surfactant/TiO$_2$ dispersion under visible light irradiation

Jincai Zhao,[a]* Kaiqun Wu,[a] Taixing Wu,[a] Hisao Hidaka[b] and Nick Serpone[c]

[a] Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, China
[b] Department of Chemistry, Meisei University, 2-1-1 Hodokabo, Hino, Tokyo 191, Japan
[c] Department of Chemistry and Biochemistry, Concordia University, Montreal H3G 1M8, Canada

The photodegradation of a cationic dye, Malachite Green (MG), is examined both in an anionic surfactant sodium dodecylbenzene sulfonate (DBS)/TiO$_2$ dispersion and in a cationic surfactant hexadecytrimethylammonium bromide (HTAB)/TiO$_2$ dispersion under visible irradiation ($\lambda > 470$ nm). In the absence of surfactants, MG is difficult to degrade in aqueous TiO$_2$ dispersion, owing to its poor solubility in water and low adsorption on the surface of TiO$_2$ particles. Addition of surfactants enhances the solubility and adsorption ability of MG and hence accelerates significantly the MG degradation rate in aqueous TiO$_2$ dispersions. The MG degradation rate reaches a maximum when the concentration of DBS added is at its c.m.c. According to the adsorption characteristics of the ionic surfactant molecules, the degradation rate of MG decreases with increases in the pH of DBS/TiO$_2$ dispersions, while the degradation of MG is more rapid at higher pH ranges in HTAB/TiO$_2$ dispersions. These results confirm and reinforce that the adsorption of dyes molecules upon the TiO$_2$ particle surface is a prerequisite for TiO$_2$-assisted photodegradation under visible irradiation and the degradation takes place at the TiO$_2$ particle surface, rather than in the bulk solution. The photodegradation kinetics of the dyes in surfactant/TiO$_2$ dispersions under visible irradiation obeys the Langmuir–Hinshelwood model. Evidence for the generation of active ˙OH radicals is obtained using spin-trapping (DMPO) EPR spectroscopy.

In the past decade, the TiO$_2$-photocatalytic degradation of organic pollutants under UV irradiation has proven to be a very effective process, which can lead to the complete mineralization of organic substrates.[1–4] However, the photocatalyst TiO$_2$ is a semiconductor with a bandgap of 3.2 eV in anatase form and only absorbs light with wavelengths below 380 nm to generate electron–hole pairs, which initiates photodecomposition.[5] Unfortunately, UV light sources are generally expensive and not easy to obtain technologically for applications. UV light in solar irradiation is $<5\%$ and is too low to achieve significant photodegradation over a short time.

Recently, we[6–8] and Kamat and co-workers[9,10] reported that dyes can undergo photodegradation under visible irradiation in aqueous TiO$_2$ dispersions and when preadsorbed on TiO$_2$ particles, which not only leads to photobleaching but also causes a complete decomposition of the dyes to evolve CO$_2$.[7] The photodegradation pathway under visible irradiation is different from that under UV irradiation in the TiO$_2$ dispersion. In the former case, the dyes, rather than TiO$_2$ particles, are excited by visible light to appropriate singlet or triplet states and then the exited dye injects an electron into the conduction band of TiO$_2$ semiconductor to form a cation radical. The injected electron can reduce the oxidants, usually O$_2$ adsorbed on the TiO$_2$ particle surface, to yield oxidizing species, such as O$_2$˙$^-$, ˙OOH and/or ˙OH radicals, that initiate the photodegradation.

It was also noted that the cationic dye, Rhodamine B, is difficult to adsorb on the surface of TiO$_2$ particles in acidic colloidal TiO$_2$ solutions and hence can not undergo photoinduced electron transfer from the exited state to the conduction band. Addition of an anionic surfactant can lead to a coadsorption of surfactant molecules with the dyes and therefore enhance the electron transfer.[11]

Generally, the adsorption of dyes on the surface of TiO$_2$ particles is indispensable for degradation of dyes.[7] However, many dyes used in industry are difficult to dissolve in water and hence do not adsorb readily on the hydrophilic surface of TiO$_2$ particles. In this work, the photodegradation of a cationic dye, Malachite Green (MG), was examined in aqueous TiO$_2$ dispersions under visible irradiation. MG has a low solubility in water and readily forms agglomerates. Consequently, degradation of MG is very slow in aqueous TiO$_2$ dispersions. Surfactants as solubilization and coadsorption reagents are added to the aqueous TiO$_2$ dispersion to enhance the solubility of MG in water and the adsorption of MG on the TiO$_2$ surface. The effect of the concentration of surfactants added and the pH of the TiO$_2$ dispersions on the degradation rate of the dyes were measured. The difference of the effect between an anionic surfactant DBS and a cationic surfactant HTAB on the degradation rate was also compared. The photodegradation kinetics of MG in aqueous surfactant/TiO$_2$ dispersions is discussed. The generation of active ˙OH radicals in the presence and absence of surfactants was also observed in the photodegradation under visible light irradiation.

Experimental

Materials

TiO$_2$ photocatalyst (P25, 90% anatase, specific surface area 50 m^2 g^{-1}) was used as kindly supplied by Degussa Malachite Green (MG), hexadecytrimethylammonium bromide (HTAB) and sodium dodecylbenzenesulfonate (DBS), were of laboratory reagent grade and used without further purification. Doubly deionized and distilled water was used throughout this study.

Photoreactor and light source

A 500 W halogen lamp (Institute of Electric Light Source, Beijing) was positioned within a cylindrical Pyrex vessel. A Pyrex jacket with water circulation was used to cool the lamp. A light filter to cut completely light below 470 nm was placed outside the Pyrex jacket to guarantee irradiation with visible light.

Malachite Green (MG)
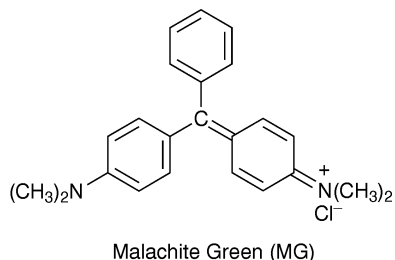
Procedures

An aqueous TiO_2 suspension was prepared by adding 50 mg TiO_2 (P25) powder to 50 cm^{-3} of solutions containing dye and DBS at appropriate concentrations. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure adsorption/desorption equilibrium. At given irradiation time intervals, the samples (4 cm^{-3}) were removed and then centrifuged and filtered with a Millipore filter (pore size 0.22 μm) to separate the TiO_2 particles. The filtrate was analyzed by observation of the UV–VIS spectrum of MG at 607 nm with a Shimadzu-1600A spectrophotometer. For reactions at different pH values the initial pH of suspensions was adjusted by adding NaOH or HCl. A Brucker Model ESP 300E spectrometer was used to detect EPR signals. The irradiation light source ($\lambda = 532$ nm) was a Quanta-Ray Nd : YAG laser system, setting: center field = 3486.70 G; sweep width = 100.0 G; microwave frequency = 9.82 GHz; power = 5.05 mW.

Results and Discussion

Fig. 1 shows the photodegradation of MG under different conditions. No changes in the MG concentration was observed after visible irradiation for 6 h in the absence of TiO_2 particles [curve (a)]. MG was also scarcely degraded in a DBS solution without photocatalyst [curve (b)]. Addition of TiO_2 particles led to some aggregation of MG (ca. 30%) as shown by a decrease in the MG concentration measured in the bulk solution before irradiation. However, the MG concentration increased with increasing irradiation time in the initial 30 min of irradiation and then decreased gradually with further irradiation. This complicated change of MG concentration in the bulk solution may be due to aggregation of MG molecules leading to poor solubility rather than degradation. Upon addition of TiO_2 particles as crystal nuclei, a mixed aggregate of MG and TiO_2 particles form, leading to a decrease in the MG concentration in the bulk solution. With increasing irradiation time, some MG molecules redissolve in the solution to cause an increase in the MG concentration
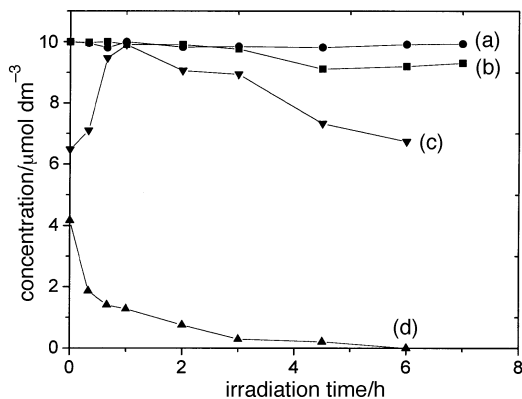
and some aggregates of MG are generated and/or a few molecules are decomposed gradually with further irradiation and hence the MG concentration decreased slowly. In this case, the degradation of MG was very slow even in the presence of TiO_2 photocatalyst. Addition of an anionic surfactant, DBS, increased the solubility of MG in the aqueous solution and enhanced significantly the adsorption and the photodegradation rate of MG on the TiO_2 surface. No aggregates of MG were generated during the photodegradation process. After visible irradiation for 4 h, MG disappeared completely and the MG molecules adsorbed on the TiO_2 surface were also degraded as evidenced by the complete discoloration of the TiO_2 surface. As a surfactant, DBS, at appropriate concentrations, can help MG disperse in the aqueous TiO_2 dispersion. The sulfonate moiety in the DBS molecule is very readily and strongly adsorbed on the surface of TiO_2 particles in the aqueous dispersion,[12,13] and therefore addition of DBS causes dye molecules to adsorb on or near to the TiO_2 surface and enhance the electron transfer from the coadsorbed dye to the TiO_2 particles under visible light irradiation, leading to the degradation of dye molecules.

The effect of the concentration of DBS added on the initial rate of MG photodegradation after irradiation for 45 min under visible irradiation is illustrated in Fig. 2. The concentration of DBS added affects significantly the MG degradation rate. The initial rate of MG photodegradation exhibited a maximum at a concentration of about 1.0×10^{-3} mol dm^{-3} which is close to the c.m.c. of DBS (1.2×10^{-3} mol dm^{-3}), which implies that MG and DBS can coadsorb efficiently on the surface of TiO_2 particles at the c.m.c. of DBS, while at concentrations greater than the c.m.c., some of the MG molecules exist in the micelles in the bulk, hindering the MG molecules approach to the TiO_2 surface to some extent and hence leading to a decrease in the initial rate of MG degradation. At lower concentrations than the c.m.c. of DBS, MG can not be coadsorbed efficiently on the TiO_2 particles since hemimicelles of DBS do not form. Details of whether the DBS molecules are degraded are not significant, but the results obtained are valid since the DBS concentration (1.2×10^{-3} mol dm^{-3}) used is much greater than the MG concentration (1×10^{-5} mol dm^{-3}).

In order to elucidate the relationship between photodegradation and adsorption, we selected DBS, an anionic surfactant, and HTAB, a cationic surfactant, to examine the photodegradation of MG in the surfactant/TiO_2 dispersion. Owing to the amphoteric behavior of TiO_2, change of pH will influence greatly the surface charge properties of TiO_2 particles. The results of the initial rate vs. pH of surfactant/TiO_2 dispersions are shown in Fig. 3. It was found that the initial rate of MG degradation and the adsorption of MG in the DBS/TiO_2 dispersion decreased simultaneously with increase
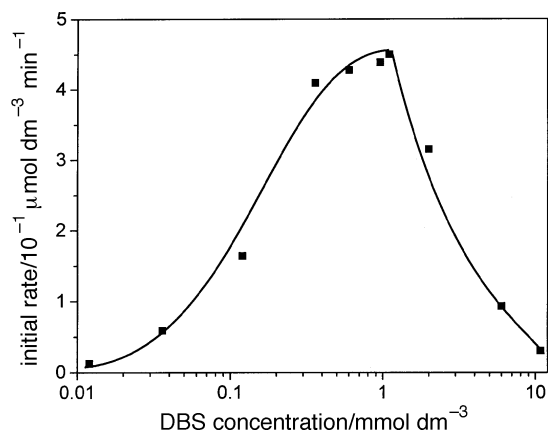

Fig. 1 Photodegradation of MG (10 μmol dm^{-3}) under visible irradiation in (a) water, (b) a DBS solution (1.2 mmol dm^{-3}), (c) TiO_2 dispersion (1 g dm^{-3}) and (d) a DBS (1.2 mmol dm^{-3})/TiO_2 (1 g dm^{-3}) dispersion

Fig. 2 Relationship between the initial degradation rate of MG (10 μmol dm^{-3}) and the concentration of DBS added
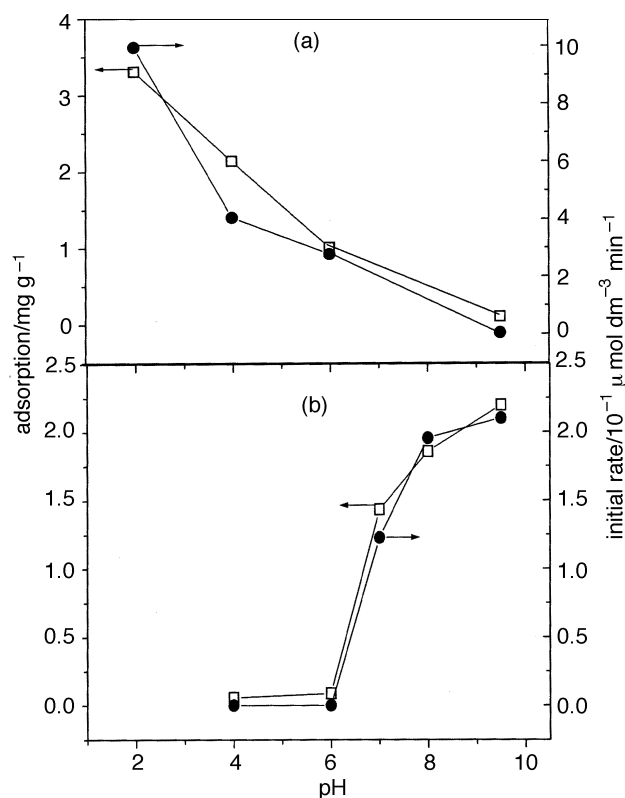
Fig. 3 Dependence of adsorption and initial degradation rate for MG (10 μmol dm^{-3}) on pH of the dispersions. (a) DBS (1.2 mmol dm^{-3})/TiO$_2$ (1 g dm^{-3}) dispersion and (b) HTAB (0.9 mmol dm^{-3})/TiO$_2$ (1 g dm^{-3}) dispersion.

in pH of the dispersion, while both the initial rate and the amount of adsorption increased with an increase in the pH of HTAB/TiO$_2$ dispersions, indicating that the pH significantly affects the coadsorption of MG and DBS or HTAB on the TiO$_2$ surface. The point of zero charge (p.z.c.) is at $pH_{pzc} = 6.8$ for the TiO$_2$ particles used in our experiments (Degussa P25).[12,14,15] The TiO$_2$ surface is positively charged in acid media (pH < 6.8) whereas it is negatively charged under alkaline conditions (pH > 6.8) as evidenced by ξ-potential measurements.[12] Owing to electrostatic effects, the adsorption of anionic DBS on the TiO$_2$ particles decreased with increasing pH, while the adsorption of cationic HTAB on the TiO$_2$ particles increased with increase in pH. Variations in the corresponding initial rate of degradation paralleled those of adsorption as shown in Fig. 3. These results confirm and reinforce that the photodegradation of dyes is closely related to the adsorption of dyes on the surface of the TiO$_2$ particles, and the degradation takes place at or near to the TiO$_2$ particle surface, rather than in the bulk solution.

Fig. 4 shows plots of the reciprocal initial rates *vs.* reciprocal initial concentrations (C_0) of MG in the presence of DBS or HTAB, respectively, at their c.m.c.s. As is known, the photodegradation kinetics of many organic compounds in TiO$_2$ dispersions under UV irradiation follows the simple Langmuir–Hinshelwood (L–H) equation:[13,15,16]

$$r = \frac{dc}{dt} = \frac{kKc}{1 + Kc} \qquad (1)$$

a linear transform of which gives:

$$\frac{1}{r} = \frac{1}{kKc} + \frac{1}{k} \qquad (2)$$

where k denotes the rate constant for the process and K represents the adsorption coefficient. As reported earlier,[7] the photodegradation kinetics of dyes in TiO$_2$ dispersions under
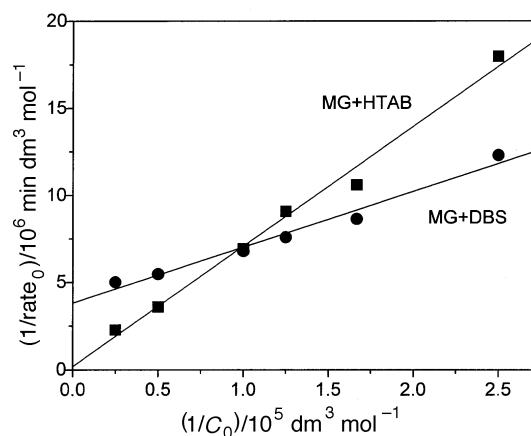

Fig. 4 Langmuir–Hinshelwood plot of MG photodegradation in DBS (1.2 mmol dm^{-3})/TiO$_2$ (1 g dm^{-3}) and HTAB (0.9 mmol dm^{-3})/TiO$_2$ (1 g dm^{-3}) dispersions under visible irradiation

visible irradiation also follow the L–H model. The linear relationships in Fig. 4 indicate that the photodegradation kinetics of MG in DBS/TiO$_2$ and in HTAB/TiO$_2$ dispersions under visible irradiation also follow the L–H model.

The light-induced degradation of MG (10 mmol dm^{-3}) under visible irradiation in the presence of various additives was also studied and the results are shown in Fig. 5. In H$_2$O$_2$ (8×10^{-2} mol dm^{-3}) homogeneous solution, MG was scarcely decomposed over several hours irradiation [curve (a)] and only to a small degree in the presence of a Fe^{3+} (40 mol dm^{-3}) [curve (b)] after 8 h photolysis. However, *ca.* 80% MG was degraded after photoreaction for 8 h in a DBS/TiO$_2$ dispersion [curve (c)] and further, when 8×10^{-2} mol dm^{-3} H$_2$O$_2$ was added to this dispersion, the degradation rate increased and nearly 90% of the MG was degraded after 6 h photolysis [curve (d)]. Meanwhile, if 8×10^{-2} mol dm^{-3} H$_2$O$_2$ was replaced by 40 mmol dm^{-3} Fe^{3+} in the dispersion, the decomposition of MG was drastically accelerated and it was completely degraded after only 1 h of irradiation [curve (e)]. The photodegradation of dyes under visible irradiation involves electron injection from excited dye molecules adsorbed on the TiO$_2$ surface into the conduction band of the TiO$_2$ semiconductor [eqn. (I)].[17–20]

$$D^*_{ads} + TiO_2 \rightarrow D^+_{ads} + TiO_2(e) \qquad (I)$$
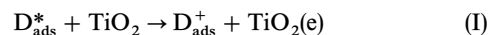
The transferred electron can subsequently be trapped by molecular oxygen, also adsorbed on the TiO$_2$ particle surface,
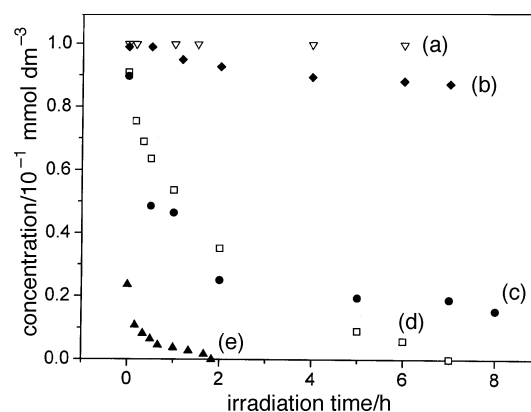

Fig. 5 Effect of additives on the degradation of MG (0.1 mmol dm^{-3}) under visible irradiation (initial pH: 3–4). (a) H$_2$O$_2$ (80 mmol dm^{-3}) homogeneous system, (b) Fe^{3+} (0.4 mmol dm^{-3}) homogeneous system, (c) aqueous heterogeneous suspensions of DBS (1.2 mmol dm^{-3})/TiO$_2$ (1 g dm^{-3}), (d) as (c) but in the presence of H$_2$O$_2$ (80 mmol dm^{-3}) and (e) as (c) but in the presence of Fe^{3+} (0.4 mmol dm^{-3}).
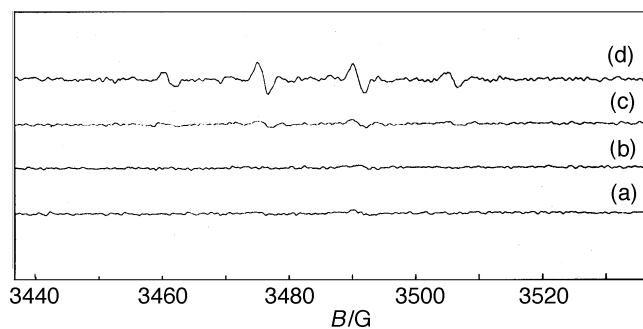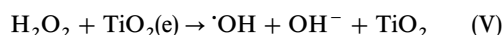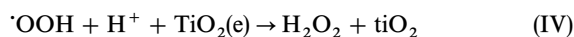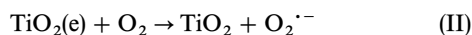
Fig. 6 DMPO spin-trapping EPR spectra. (a) MG–DBS solution after visible irradiation for 9 min, (b) MG/TiO$_2$ dispersion after visible irradiation for 9 min, (c) MG–DBS/TiO$_2$ dispersion before irradiation and (d) MG–DBS/TiO$_2$ dispersion after visible irradiation for 9 min. Volume of dispersions (0.3 cm^{-3}), MG: 10 μmol dm^{-3}, DBS: 1.2 mmol dm^{-3}, TiO$_2$: 1 g dm^{-3}, DMPO: 0.16 mol dm^{-3}, irradiation light source: laser, $\lambda = 532$ nm.

to form O$_2^{\cdot-}$ which can then generate highly active $\cdot$OOH and $\cdot$OH radicals [eqn. (II)–(V)].[21]

$$TiO_2(e) + O_2 \rightarrow TiO_2 + O_2^{\cdot-} \qquad (II)$$

$$O_2^{\cdot-} + H^+ \rightarrow \cdot OOH \qquad (III)$$

$$\cdot OOH + H^+ + TiO_2(e) \rightarrow H_2O_2 + tiO_2 \qquad (IV)$$

$$H_2O_2 + TiO_2(e) \rightarrow \cdot OH + OH^- + TiO_2 \qquad (V)$$

The radical cation of dye reacts with these reactive oxygen radicals, and/or molecular oxygen, to yield intermediates or completely mineralized products [eqn. (VI)].

$$D_{ad}^+ + \{\cdot OH, O_2^{-\cdot} \text{ and/or or } O_2\} \rightarrow$$

$$\text{degraded or mineralized products} \qquad (VI)$$
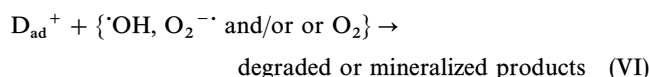
Addition of H$_2$O$_2$ enhanced the photodegradation rate of MG possibly owing to favorable generation of OH radicals [eqn. (V)]. The presence of Fe^{3+} increased the adsorption of MG on the TiO$_2$ surface as shown in Fig. 5, as well as making reaction (V) easier, with Fe^{3+} acting as a photo-Fenton catalyst,[22] and hence accelerating drastically the photodecomposition of MG.

Fig. 6 shows DMPO spin-trapping EPR spectra. There were no free radicals detected either in the MG–DBS system [curve (a)] or in the MG/TiO$_2$ dispersion [curve (b)] under visible irradiation after 9 min. No EPR peaks were observed in the MG–DBS/TiO$_2$ dispersion before irradiation [curve (c)], while the characteristic four peaks from DMPO-OH adducts with an intensity ratio of 1 : 2 : 2 : 1 appeared in the MG–DBS/TiO$_2$ dispersion upon visible irradiation and remained unchanged in intensity after irradiation for 2 min. Curve (d) shows characteristic EPR signals after 9 min irradiation. These results infer that only when both DBS and TiO$_2$ exist in the dispersion can the $\cdot$OH radical be generated under visible irradiation. In the absence of DBS, no $\cdot$OH radicals were generated, since MG molecules can not contact easily with the surface of TiO$_2$ particles and consequently the electron transfer from the dye to TiO$_2$ can not proceed, and reactions (II)–(VI) can scarcely proceed. Therefore, the photodegradation of MG was very slow and only some agglomerates separated from the dispersion.

Conclusion

MG which shows poor solubility in water can be easily degraded under visible light irradiation after addition of sur-factants to TiO$_2$ dispersions. In DBS/TiO$_2$ dispersions, the adsorption and degradation rate of MG are much greater in acidic than those in neutral and alkaline media, while in the CTAB/TiO$_2$ dispersion, the opposite effect was observed. The most appropriate concentration of DBS added is the c.m.c. for the maximum degradation rate of MG. The results confirm that the degradation proceeds at the semiconductor particle surface rather than in the bulk solution; $\cdot$OH active species are generated and participate in the photodecomposition reaction.

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