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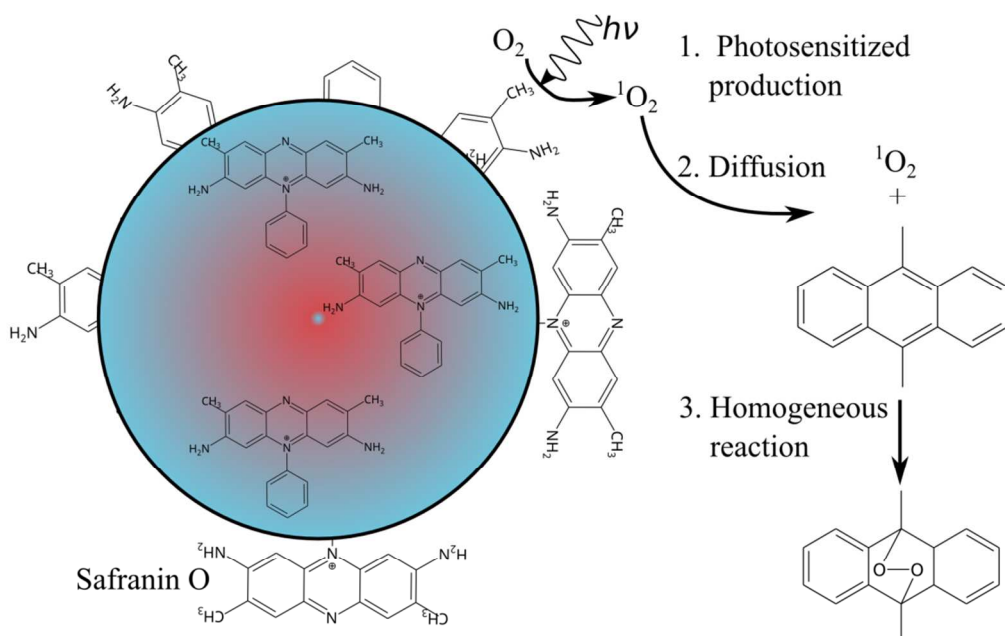


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Photosensitized oxidation of 9,10-dimethylanthracene with singlet oxygen
by using safranin O/silica composite under visible light

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Abstract

The photosensitized oxidation of 9,10-dimethylanthracene with singlet oxygen in acetonitrile was investigated using a safranin O/silica composite as heterogeneous delivery system of the photosensitizer. The only detected product was the corresponding endoperoxide (9,10-endoperoxianthracene) and its formation rate was depending of initial concentration of DMA, light intensity and the amount of composite. The kinetics of this reaction was compared to that of the reported kinetic model of photosensitized oxidations of organic compounds in homogeneous reactions. It was found that both reactions followed the same model, suggesting that the actual reaction between photoproduced singlet oxygen and 9,10-dimethylanthracene was performed in homogeneous media and the surface of the composite was not involved in the reaction.

Introduction

Ground molecular oxygen and its properties have been actively studied for more than 200 years; however, the properties of its lowest excited state have only been investigated during the last decades¹⁻³. This excited state has both electrons in the same orbital with opposite spins, it is a singlet state denoted as $^1\text{O}_2$ ($^1\Delta_g$), with a relative long lifetime (4 μs in water)⁴. Due to its electronic configuration, $^1\text{O}_2$ is an electrophilic agent, reacting preferentially with electron-rich organic molecules such as olefins, dienes, polycyclic aromatic compounds, phenols and sulfides⁵⁻⁷.

Singlet oxygen is also generated in biological systems and can be implicated in defense mechanism against viruses and bacteria⁸. This cytotoxic effect has been successfully applied in photodynamic

therapy (PDT) to kill carcinogenic cells. PDT involves administration of a tumor localizing photosensitizing agent, or photosensitizer, followed by activation of the agent with light of a specific wavelength. The ideal photosensitizer would be a chemically pure compound with preferential uptake in tumor and a strong absorption of light⁹⁻¹³.

There are several ways to produce $^1\text{O}_2$, such as chemical reaction, gas phase discharge and photosensitization reaction, being the latter route the most used, especially in organic synthesis^{14,15}. It is important to note that the best way to produce singlet oxygen is by immobilizing the photosensitizer in an insoluble matrix to carry out the organic synthesis in heterogeneous medium avoiding problems related to catalyst separation, usually encountered in homogeneous medium^{6,15,16}. Concerning selective photo-oxidation reactions (i.e. photo-oxidation with $^1\text{O}_2$), several articles have been published highlighting its importance in fine chemical production under mild conditions^{1,6,7,15,17-20}. However, relevant aspects to be taken into account for a photosensitizer/support system are its activity to generate singlet oxygen, selectivity and stability in the reaction medium for a specific application in fine chemicals synthesis.

Safranin O or basic red 2 belongs to the family of phenazium dyes, which has found many biological applications^{21,22} as well as in photooxidation of organic compounds^{23,24}. In our previous work, we successfully linked methylene blue, toluidine blue, neutral red (NR), and safranin O (SF), into a silica matrix by using an ultrasound irradiation method²⁵. The entrapped dyes on silica were evaluated in $^1\text{O}_2$ generation, among these four different types of dye-doped silica composites, the SF/SiO₂ composite showed the most efficient delivery of $^1\text{O}_2$ quantified by the ability to convert and 9,10-dimethylanthracene (DMA) in its corresponding endoperoxide²⁵.

The aim of the present work was to study the photooxidation process occurring between DMA and singlet oxygen produced by irradiation with visible light of a SF/SiO₂ composite in air atmosphere. In particular, it was interesting to verify the operation conditions under which the formation of the endoperoxide occurs such as initial concentration of DMA, light intensity and the amount of composite.

Experimental section

Preparation and characterization of the safranin O/silica composite.

The SF/SiO₂ composite was synthesized as follows: as silica source was used tetraethyl orthosilicate (TEOS), safranin O (SF) as photosensitizer, both were purchased from Sigma-Aldrich and used without further purification. Ethanol (HPLC grade, Fermont) and double distilled water were used as solvent and ammonium hydroxide (NH₄OH, Fluka) was used as catalyst. The SF/SiO₂ composites were

synthesized using a one-step Stöber method²⁶ for the generation of monodispersed particles of silica, where the dye was incorporated since the preparation of gel precursor^{27,28}. Briefly, two solutions were prepared, one containing TEOS and ethanol (solution 1) and another one with NH₄OH, water, and SF (solution 2). Then, solution 1 was poured drop by drop into solution 2 under magnetic stirring and the mixed solution was placed in ultrasonic irradiation during 10 min. Finally, the precursor solution of the composite material was aged for 12 h under vigorous agitation. The obtained powders were completely dried under vacuum at 318 K. The molar ratios used in the preparation of the composites were 1/20/0.1/30 for TEOS/water/NH₄OH/ethanol, and the nominal dye concentration was 1×10^{-6} mol SF/g of SiO₂.

Photochemical evaluation

The photosensitized oxidation of 9, 10-dimethylanthracene (DMA) was carried out in acetonitrile (ACN, HPLC grade, Fermont) using a solar simulator (Newport model 67005) equipped with a 150 W Xe lamp with a maximum emission around 460 nm, and a power source which allow to change light intensity of the lamp. The reactions were carried out in an 80 mL batch reactor separated 20 cm from the source. The temperature was kept constant at 298 K, and the incident light was filtered by using a coloured glass filter (Shimadzu GF-VY43), in order to cut out light below 410 nm and eliminate any photochemical reaction of DMA (Fig. 1). Visible Light intensity was measured using a digital light meter (A. W. Sperry SLM-110) and the measured light intensity was 1.5 mW/cm^2 (I_0) at 20 cm from the source. Typically, the initial concentration of DMA was 7.3×10^{-5} mol/L, the composite loading was 0.5 g/L and I_0 was 1.5 mW/cm^2 . Reaction samples were taken at fixed time intervals and the SF/SiO₂ composite was removed using a PTFE membrane filter (Micropore, 0.45 μm) prior to analysis. DMA concentration was measured using a spectrofluorometric method (Shimadzu model RF-5301PC), using an excitation wavelength of 270 nm. The DMA concentration was calculated using a calibration curve following the decrease of light emission of DMA at 400 nm (see Fig. S1).

Results and discussion

Figure 1 shows the UV-Vis diffuse reflectance spectrum of SF/SiO₂ composite as prepared by a modified sol-gel method. The composite presented a slight pink color with a maximum of absorption at 520 nm. After being exposed to daylight or reacted with DMA (see Fig S2 in the supporting information), it remained the same color and homogeneity. Figure 2 shows the FT-IR spectra of: a) as-prepared SiO₂, b) SF/SiO₂ ($[\text{SF}] = 1 \times 10^{-6}$ mol/g SiO₂) and c) safranin O. In the case of the SiO₂, it

can be observed several bands, *i.e.* at 1200, 1100, 800, and 460 cm^{-1} , which were attributed to Si–O–Si vibrations and the band at 960 cm^{-1} corresponds to the Si–OH vibration²⁹. The main absorption bands of SF (Fig. 2c) at 1610, 1530, 1490 and 1330 cm^{-1} were assigned to the =N⁺ cation, the heterocyclic skeleton, and to the –CH₃ symmetric and asymmetric bending vibrations, respectively³⁰. As can be seen in Fig. 2, the spectrum of the SF/SiO₂ composite was quite similar to that of SiO₂ due to the low concentration of SF in the composite (Fig. 2b), so that the main absorption bands of SF cannot be detected; however, it was observed a slight change on the intensity of the bands at 560, 960, and 1200 cm^{-1} , which could be attributed to a weak interaction between SF and the SiO₂ matrix. However, the most rational explanation is that the dye is only embedded (entrapped) between the intercrystalline spaces of the silica. As it is well-known, to chemically bind the dye to the silica, functional groups such as hydroxyl, amino, thiol, etc, are required, which were not introduced during the preparation of our composites³¹⁻³².

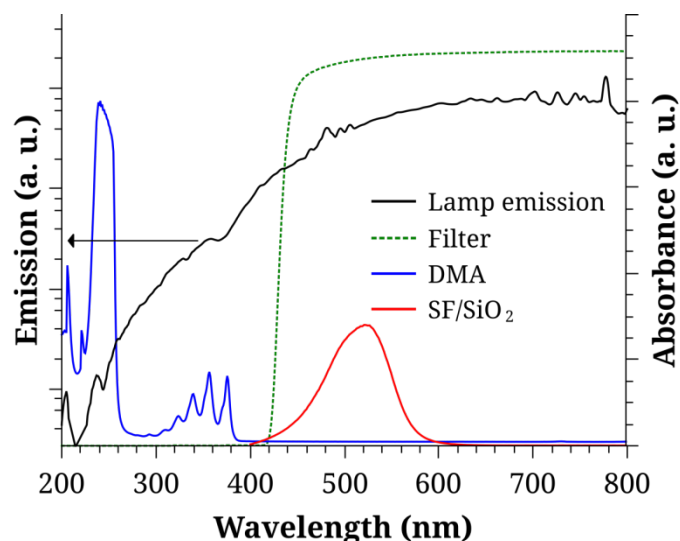


Figure 1: UV-Vis diffuse reflectance spectrum of SF/SiO₂ composite (1×10^{-6} mol SF/g of SiO₂), emission spectra of Xe lamp, spectral characteristics of the cutoff filter used and absorption spectra of DMA (7.3×10^{-5} mol/L in ACN)

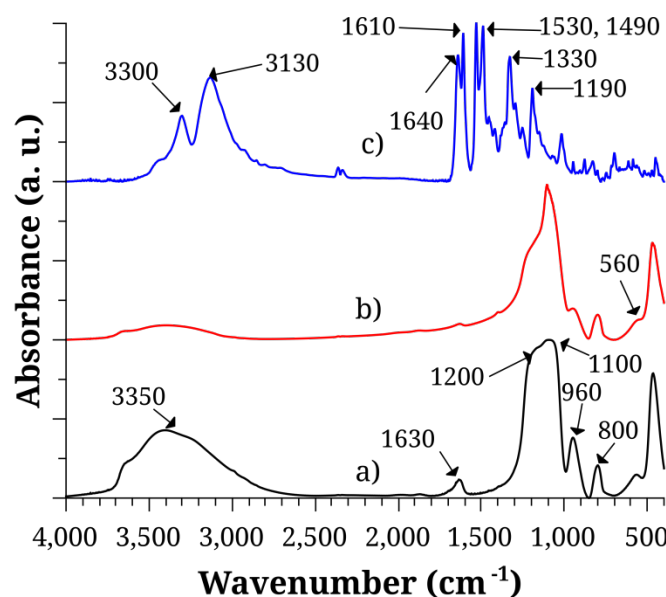


Figure 2: FT-IR spectra of: a) as-prepared SiO₂, b) SF/SiO₂ composite and c) safranin O powder.

The photosensitized oxidation of DMA was carried in a slurry system containing DMA dissolved in acetonitrile and irradiated with visible light (410-800 nm). No appreciable reaction of DMA was observed either in absence of visible light or SF/SiO₂ composite. Figure 3A shows the concentration profiles as a function of time of irradiation at different initial concentration of DMA. As expected the DMA conversion was faster at lower initial concentration of DMA (2.4×10^{-5} – 23×10^{-5} mol/L) and it was almost completed in 120 min, while at higher concentration (58.2×10^{-5} mol/L) was 75%. At lower concentrations, all data seem to follow an apparent first order kinetic, but at higher concentration (58.2×10^{-5} mol/L) there was a change in the profile to an apparent zero order kinetics. This change can be also observed in Fig S3 of the supplementary information where all the concentration profiles were fitted to first-order model. It can be seen that as DMA concentration was increased, the goodness of the fitting decreased pointing out to a change in the kinetics.

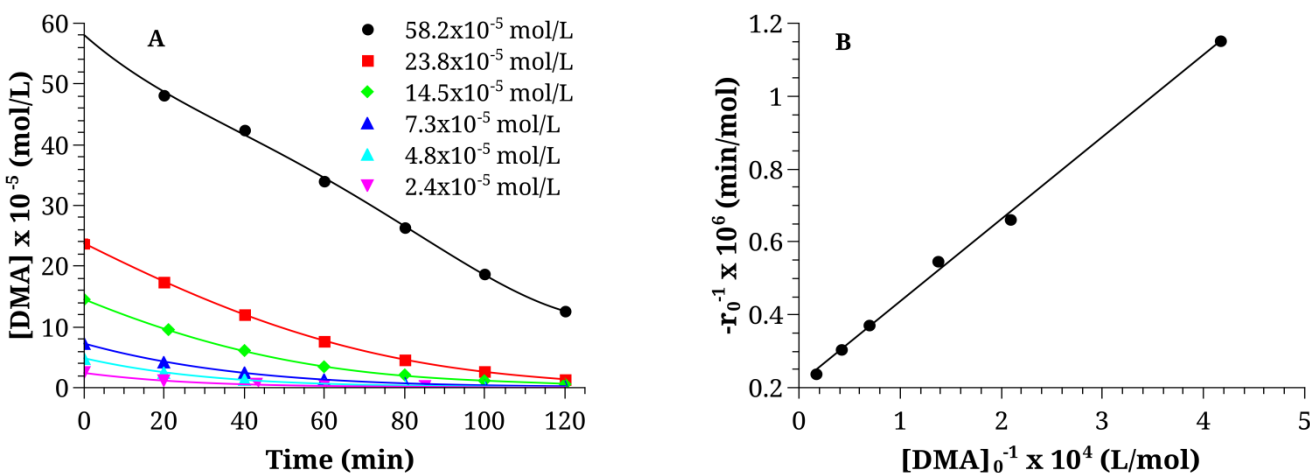


Figure 3: A) Concentration of DMA versus time, using different initial concentrations of DMA. B) Inverse of the initial reaction rate versus the inverse of the initial concentration of DMA. $C_{\text{Comp}} = 0.5$ g/L, $I = 1.5$ mW/cm².

These results can be explained by the following kinetic equation, which has been applied in photosensitized oxidation in homogeneous media^{8,33}:

$$\Phi_{OX} = \frac{r_{OX}}{I_a} = \frac{\Phi_A k_r^A [A]}{k_d + k_A [A]} \quad (1)$$

Where Φ_{OX} is the quantum yield of oxidation of substrate, Φ_A represents the quantum yield of ¹O₂ formation, k_A is the rate constant for global reaction of ¹O₂ with substrate (including physical quenching and chemical reaction), k_r^A is the rate constant for chemical reaction of substrate A, k_d is the first-order decay rate of singlet oxygen in solvent and I_a is the rate constant for the formation of excited states of the photosensitizer under continuous illumination. According to Eq. 1, when $k_d \gg k_A [A]$ or $k_A [A] \gg k_d$ the rate of oxidation would be first or zero order respectively with respect to A. Eq. 1 can be rearranged to give³³:

$$r_{OX}^{-1} = (I_a \Phi_A f_r^A)^{-1} \left[1 + \frac{k_d}{k_A [A]} \right] \quad (2)$$

Where $f_r^A = k_r^A / k_A$ is the fraction of reactive quenching of ¹O₂ by substrate A. Additionally, the linear plot of the inverses of $-r_0$ and $[A]$ in Eq. 2 should give^{8,33}:

$$\frac{\text{slope}}{\text{intercept}} = \frac{k_d}{k_A} = \beta_A \quad (3)$$

Where β_A represents the concentration at which the decay of singlet oxygen in the solvent alone equals

the decay due to quenching by A, i.e., it is the half-quenching concentration⁸. To corroborate this behaviour, the inverse of initial rate ($-r_0$) of DMA transformation was plotted against the inverse of initial concentration, shown in Fig. 3B. As can be seen, there was a linear relationship between the inverses of $-r_0$ and C_0 . From the lineal fitting of these variables seen in Figure 3B, the calculated value of β_A was 1.07×10^{-4} mol/L, which is in agreement with the reported values of this parameter for the photosensitized oxidation of DMA in acetonitrile in homogeneous media^{33,34}. Also, using reported values of k_d ($1.42 \times 10^4 \text{ s}^{-1}$)³³ and Eq. 3, the calculated value of k_A was 1.33×10^8 L/mol s. This value of k_A is also in agreement with the values reported previously³⁴.

In other works related to the photosensitized oxidation of organic compounds in heterogeneous media, the reaction kinetics has been explained with the well-known approach of Langmuir-Hinshelwood (LH) equation³⁵. Nevertheless, the LH approach is devoted to the effect of adsorption and surface reactions steps. On the contrary, the homogeneous approach described by equation 1, involves photophysical aspects of $^1\text{O}_2$ generation as well as the homogeneous reactions of $^1\text{O}_2$ with the substrate.

According to our results, it can be suggested that the photosensitized oxidation of DMA was independent of the phase where the photosensitizer is located, i.e. the surface of the composite was not involved in DMA or oxygen species adsorption. During all the experiments, DMA adsorption on the surface of SF/SiO₂ composite was not detected, and in the other hand, singlet oxygen lifetime in acetonitrile is $70 \mu\text{s}$ ³³. This lifetime is long enough to allow the singlet oxygen to be generated by the composite, diffuse in the solvent and reacts with dissolved DMA. Therefore, it is suggested that the photooxidation of DMA could be performed in three steps (Fig. 4): the first step is the photosensitized production of $^1\text{O}_2$ near the surface of the composite; the second step is the diffusion of $^1\text{O}_2$ from the surroundings of the surface to the solvent and the third step is the homogeneous reaction between $^1\text{O}_2$ and DMA.

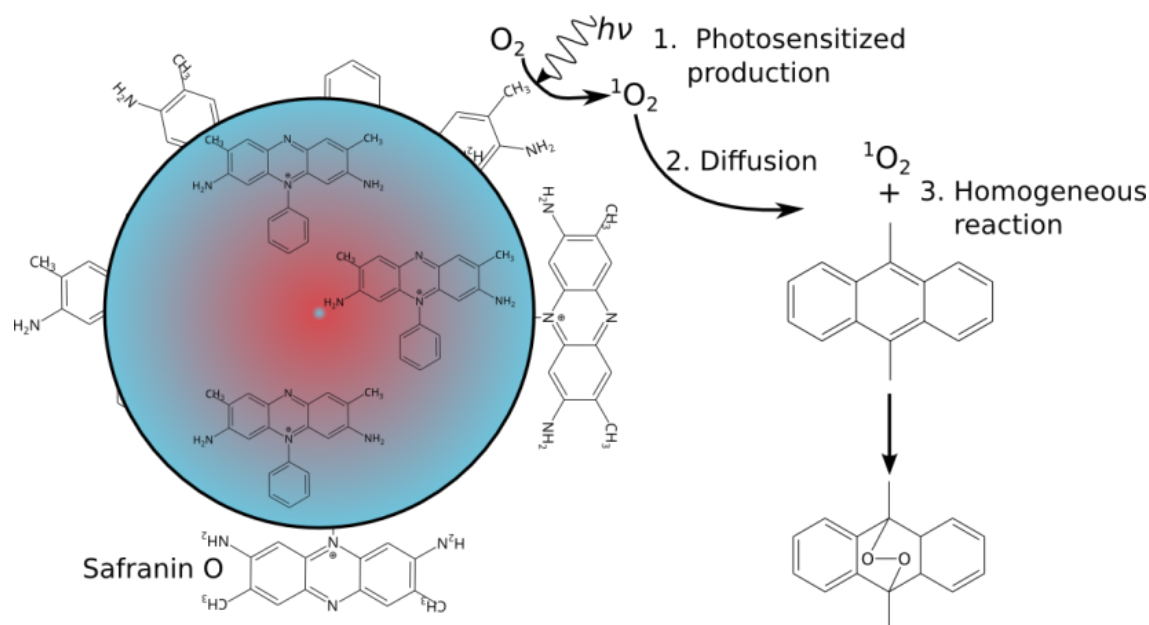


Figure 4: Schematic representation of the photosensitized oxidation of DMA using SF/SiO₂ composite.

In a second set of experiments, the influence of the light intensity over the photosensitized oxidation of DMA was investigated. As expressed earlier, at lower initial concentrations of DMA, the condition $k_d \gg k_A[A]$ is met and Eq. 1 can be simplified to

$$r_{OX} = k_1'[A] \quad (4)$$

Where $k_1' = k_r^A I_a \Phi_A / k_d$ is a pseudo first order constant. According to Eq. 4, there is a lineal relationship between r_{OX} and light intensity. In Fig. 5A is shown the relative concentration of DMA vs. time for different light intensities. The conversion at 120 min was proportional to the light intensity and for the higher light intensity was almost 98 %. To verify the validity of Eq. 4, k_1' was calculated fitting the concentration profiles of DMA to a first-order kinetics (see Fig. S4 in the supporting information) and plotted versus the relative light intensity. As observed in Fig. 5B, there was a linear relationship between k_1' and the relative light intensity, which is consistent with Eq. 4. It is well-known that the reaction rates in photo-oxidation reactions can be linear at low light intensities, square root- dependent at intermediate light intensities and at high light intensities it maintains constant³⁶.

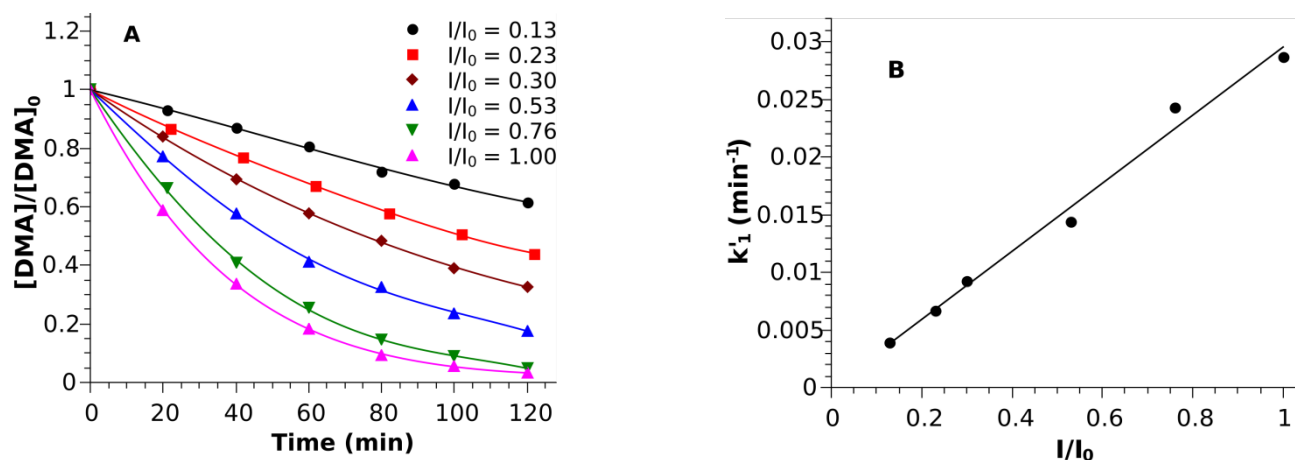


Figure 5: A) Relative concentration of DMA vs. time at different light intensities. B) Observed experimental constants in function of light intensity. ($C_0 = 7.3 \times 10^{-5}$ mol/L and $C_{Comp}=0.5$ g/L).

The influence of the composite concentration on DMA conversion is reported in Fig. 6. It is clear that at increasing the composite concentration, a faster consumption of DMA is observed. Note that a linear relationship between the pseudo first order constant (k_1) and the composite concentration was clearly observed in the range of 0.125 to 0.8 g/L, after this value, a screening effect of excess of particles results preventing an efficient incidence of light on the photosensitizer, as observed in other heterogeneous systems³⁷. These results indicated that the singlet oxygen required to react with DMA is closely related with the amount and distribution of safranin O on the support, therefore, this information is specific for each composite and useful for scaling proposes.

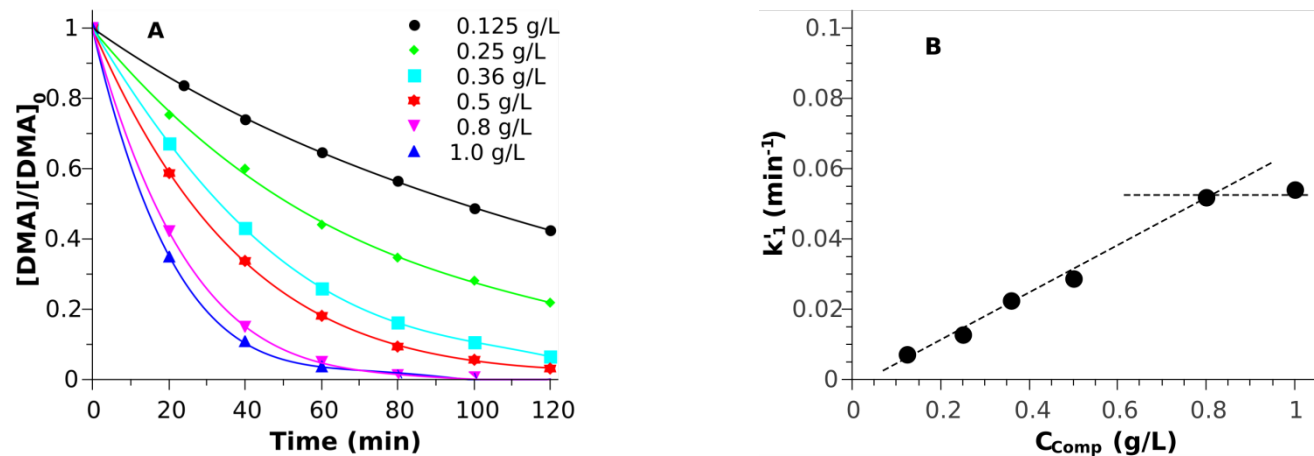


Figure 6: A) Relative concentration of DMA in function of composite loading. B) Observed experimental constants versus the composite loading. ($C_0 = 7.3 \times 10^{-5}$ mol/L, $I = 1.5$ mW/cm²).

Conclusion

Safranin O was successfully incorporated to a silica matrix by a simple and green sol-gel method. The composite SF/SiO₂ presented a high activity and stability to the conversion of DMA under different operation conditions. At lower initial concentrations of DMA (2.4×10^{-5} – 23×10^{-5} mol/L), it was observed a first order kinetics, while at higher concentrations (58.2×10^{-5} mol/L) it seemed to move to zero order kinetics. The obtained results were fitted in a typical kinetic equation employed in homogeneous medium. Light intensity variation showed a linear relation between the observed rate constant and relative to I/I_0 . In the same way, at increasing the amount of composite a linear relation with the observed rate constant was clearly observed. Our results revealed that singlet oxygen reacts in solution with DMA forming the corresponding endoperoxide similarly as in homogeneous medium. These preliminary results indicated that safranin O has a potential to be used in other chemical transformations but it is necessary to know in detail what about the singlet oxygen quantum yield under different solvents and the effect of the type of support.

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