Photodegradation of Malachite Green in the Presence of Fe^{3+}/H_2O_2 under Visible Irradiation

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The photodegradation of malachite green (MG) in the presence of Fe^{3+} and H_2O_2 under visible light irradiation ($\lambda>450$ nm) is reported in comparison with that in the dark. It was found that the visible irradiation can accelerate significantly the Fenton degradation of dyes, which provides possibly a preferable approach for the treatment of dye pollutants in wastewater.

In recent years, there is great interest in the possibility to use Fenton-type reactions in the dark[1-3] and under UV light irradiation[4,5] in the field of advanced oxidation technologies for the treatment of organic pollutants *via* homogeneous system. Fenton reactions in the dark are relatively slow, it is now known that UV irradiation can accelerate significantly the Fenton degradation of organic pollutants.[4,5] The mechanism of the increase in the oxidizing power of Fenton-type reaction under UV irradiation has been studied by several researchers.[6,7] To our knowledge, however, few studies was reported on the photo-Fenton reactions under visible irradiation.

We have reported the photocatalytic degradation of a dye, malachite green (MG), in the presence of TiO_2 semiconductor particles under visible light irradiation,[8] in which the addition of Fe^{3+} and H_2O_2 increased greatly the photodegradation rate of MG. In this work, the photodegradation of MG in the presence of Fe^{3+}/H_2O_2 was examined to reveal whether the visible light irradiation ($\lambda>450$ nm) has a beneficial effect on the degradation of dyes and to elucidate the mechanistic details that led to this effect.

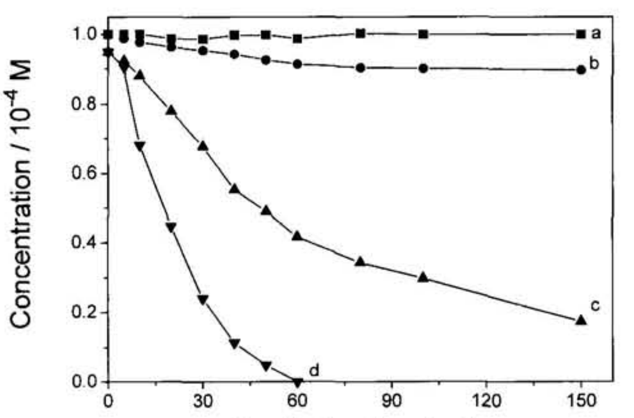

Figure 1 Degradation of MG (0.2 mmol dm^{-3}) under different conditions (initial pH:2.9). (a) H_2O_2 (0.44 mol dm^{-3}) homogeneous system under visible irradiation, (b) Fe^{3+} (0.4 mmol dm^{-3}) homogeneous system under visible irradiation, (c) in the presence of H_2O_2 (0.44 mol dm^{-3}) and Fe^{3+} (0.4 mmol dm^{-3}) in the dark, (d) in the presence of H_2O_2 (0.44 mol dm^{-3}) and Fe^{3+} (0.4 mmol dm^{-3}) under visible light irradiation.

Figure 1 shows the degradation of MG under different conditions. Irradiation experiments were carried out using a 500 W halogen lamp (Institute of Electric Light Source of Beijing) as visible light source and a light filter was used to cut completely light below 450 nm to guarantee irradiation with visible light. A glass thimble with water circulation was used to avoid overheating. In typical experiments, a solution (5 ml) containing MG (0.2 mmol dm^{-3}) and other additives (H_2O_2 or/and Fe^{3+}) was contained in a pyrex glass vessel and let it react under visible light irradiation or in the dark at room temperature. At given time intervals, the changes in the MG concentration were analyzed on Shimadzu 1600A Spectrophotometer. In H_2O_2 homogeneous solution, MG was scarcely photodecomposed over several hours of visible irradiation [curve a] and only degraded to a small degree in the presence of Fe^{3+} [curve b] after 150 min of photolysis. When both Fe^{3+} and H_2O_2 were present but in the dark (curve c), MG was degraded slowly *via* an apparent first-order kinetics with a rate constant of 2.4×10^{-4} s^{-1} and about 80% MG was decomposed after the dark reaction for 150 min. However, the degradation of MG in the presence of Fe^{3+}/H_2O_2 under visible light irradiation [curve d] showed a much greater rate, which occurs also *via* an apparent first order kinetics with a rate constant of 1.0×10^{-3} s^{-1} and MG disappeared completely after visible light irradiation for 60 min. The experimental results indicate that visible irradiation accelerates greatly the photodegradation of MG .

The reaction of a ferrous or a ferric salt with H_2O_2 in the dark can produce •OH radicals as shown in eqns.1 and 2[9] and reaction (1) was more quickly than reaction (2). Pignatello et.al.[10] attributed the main advantage of UV light irradiation to the regeneration of the consumed Fe^{2+} and the additional generation of •OH through eqn.3:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O \quad k = 76\ M^{-1}\ s^{-1} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet OOH + H^+ \quad k = 0.03\ M^{-1}\ s^{-1} \qquad (2)$$

$$Fe(OH)^{2+} + h\nu \rightarrow \bullet OH + Fe^{2+} \quad \text{(UV light)} \qquad (3)$$

On the basis of the conventional framework of Fenton reaction and the experimental observations, we suggest a probable reaction mechanism of the photo-Fenton degradation of MG under visible irradiation as follows:

$$MG + h\nu \rightarrow MG^* \quad \text{(visible light)} \qquad (4)$$

$$MG^* + Fe^{3+} \rightarrow MG^+ + Fe^{2+} \qquad (5)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O \qquad (1)$$

$$MG^+ + \bullet OH \text{ and/or } O_2 \rightarrow \text{degraded or mineralized products} \qquad (6)$$

Upon visible light irradiation, dye can absorb the visible light which subsequently lead to an electron transfer from the excited dye molecule to Fe^{3+} (eqn. 4 and 5). Formation or regeneration of Fe^{2+} accelerates the production of •OH radicals (eqn.1) and hence enhances the degradation rate of dye.

According to the proposed mechanism, a substance which can not absorb visible light should not proceed the above reactions (eqns.4 and 5), so we selected sodium dodecylbenzene (DBS) with little absorbency at wavelengths above 300 nm and

Table 1. TOC variation in the degradation of MG and DBS

Reactants	Time	TOC	Note
MG	0min	47.54	
Fe^{3+}	140min	23.78	dark reaction
H_2O_2	140min	0	visible irradiation
DBS	0h	23.86	
Fe^{3+}	16h	8.06	dark reaction
H_2O_2	16h	8.07	visible irradiation

MG: 0.2 mmol l^{-1}, Fe^{3+}: 0.4 mmol l^{-1}, DBS:0.1 mmol l^{-1}, H_2O_2 0.44 mol l^{-1}.

carried out the experiment again under the otherwise identical conditions as Figure 1. The degradation of DBS was detected by the changes in total organic carbon (TOC) as shown in Table 1. The almost same TOC changes were observed under visible light illumination and in the dark after reaction for 16 h. By the contrast, the TOC variation of MG under visible light irradiation was much greater than that in the dark after 140 min of reaction. These results indicate that it must be a substance can absorb visible light that will proceed the first two steps of the proposed mechanism. We next investigated whether the conversion of Fe^{3+} to Fe^{2+} under visible irradiation is more than that in the dark reaction by detection of the produced Fe^{2+} concentration. The maximum concentration of Fe^{2+} formed was 0.17 and 0.12 mmol dm^{-3} under visible irradiation and in the dark reaction, reapectively. The time to reach the maximal concentration was 8 min and 12 min, respectively. These experimental results indeed supported the proposed mechanism (eqn. 5) that additional conversion of Fe^{3+} to Fe^{2+} occurs under visible irradiation .

The spin-trapping EPR technique has proven to be useful in detecting radical species and hence to examine the photo-induced electron transfer[11] and the photocatalytic reaction pathways.[12,13] Figure 2 illustrates the DMPO spin-trapping EPR spectra under different conditions. The intensity of the characteristic four peaks from DMPO-OH adducts became stronger obviously when the reaction system was exposed to the visible light illumination compared to those in the dark reaction. It is easy to explain that visible light irradiation leads to the additional generation of Fe^{2+} and consequently the amount of •OH radicals formed under visible light irradiation is more than that in the dark reaction .

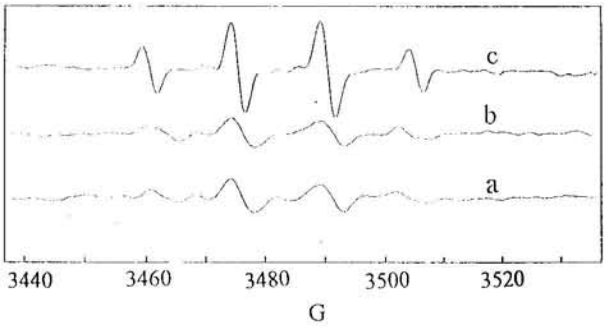

Figure 2. DMPO spin-trapping EPR spectra. (a)MG-Fe^{3+}/H_2O_2 homogeneous system before visible irradiation, (b) the same system as (a) in the dark for 2 min and (c) the same system as (a) after visible irradiation for 2 min.
Volume of solution: 0.3 cm^{-3}, MG: 0.2 mmol dm^{-3}, Fe^{3+} : 0.4 mmol dm^{-3}, H_2O_2: 0.44 mol dm^{-3}, DMPO: 0.16 mol dm^{-3}, irradiation light source: laser λ=532 nm.

In order to testify further the proposed mechanism, we added different concentrations of $C_2O_4^{2-}$ to the reaction system to make the radio of $C_2O_4^{2-}$/Fe^{3+} is 1, 2, 3, 5 and 100 and let it react in the dark, under UV irradiation and visible irradiation, respectively. The degradation rate of MG decreased to some extent under the three conditions in comparison with the $C_2O_4^{2-}$ -free system. With increasing the concentrations of $C_2O_4^{2-}$, the degradation rate exhibited a constant under UV irradiation because UV light can excite the complex of Fe^{3+} with $C_2O_4^{2-}$ yielding Fe^{2+},[14] while it became much slower under visible irradiation since the electron transfer from the excited MG to Fe^{3+} is retarded due to the complex of Fe^{3+} with $C_2O_4^{2-}$. And the degradation of MG was scarcely observed with increase in the concentration of $C_2O_4^{2-}$ in dark reaction since both the formation of Fe^{2+} and the reaction of Fe^{3+} with H_2O_2 can not proceed owing to the complex of Fe^{3+} with $C_2O_4^{2-}$.

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