

Heterogeneous photocatalytic degradation of methylene blue aqueous solution under the coexistence of metalloporphyrin polymer and air

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Abstract High pressure mercury lamp (HPML) was used for irradiation, the kinetics of photocatalytic degradation of methylene blue (MB) in water with air sparging has been investigated in the presence of Polymeric[Co(II)meso-Tetra(4,4'-Biphenylbisulfony)-phenyl porphyrin]. Chemical Oxygen Demand (COD) proximately dropped by half, with the decolourizing efficiency being about 50-60% after 8 hours. The changes of the visible spectra and the kinetics curve of reaction were measured. It was observed that photocatalytic degradation of MB obey pseudo first-order reaction with the apparent first-order decay constant $k = 0.3544 \text{ h}^{-1}$, half life 1.96 h. Compared with HPML, natural sunlight (NSL) had similar effect on the photocatalytic degradation of MB. The effects of a variety of factors such as pH, irradiation sources and initial concentration of MB were discussed. MB in water could degrad within 3 h in the presence of metalloporphyrin polymer and diluted solution of hydrogen peroxide.

Keywords Photocatalytic degradation, Methylene blue, Metalloporphyrin, Kinetics

The issue of treatment of organic pollutants in water is an ever increasingly global problem because many organic contaminants are inevitable byproducts of industry and agriculture. In 1980s, the total production of synthesized dyes alone was more than 800 thousand tons per year. In the course of production and utilization, a significant amount of dye-containing wastewater was discharged into receiving water.

In recent years, several alternative oxidative degradation processes using catalytic and photochemical methods have been developed. Considerable academic interest has been focused on the photocatalytic degradation of contaminants in water with semiconductor TiO_2 . There have been many reports on the photocatalytic oxidation of organic pollutants such as dyes, pesticides, surfactants etc. in water [1-5]. During last two decades, there were also a few reports on the catalytic oxidation of organic substrate in non-aqueous solvent using metalloporphyrin as photocatalysts [6-9]. But, this is the first report on the heterogeneous photocatalytic degradation of organic pollutants in water using suspension metalloporphyrin polymer and irradiated by HPML. Moreover, the process could also be driven by NSL, significantly potential application of solar energy considering the photosensitivity of metalloporphyrin.

1. EXPERIMENTAL

1.1 Materials

Polymeric Co[meso-Tetra (4,4'-Biphenylbisulfony)phenyl-porphyrin] (Co[P(TBPSOPP)]) was prepared, purified and characterized as previously reported [10], and visible spectra of polymeric ligand exhibits a soret band at 422.1 nm, with the Q bands at 524.2, 558.7, 599.0, and 658.2 nm. The soret band varied little and the Q bands decreased from 5 to 2 with the ligand coordinating with metals. MB was obtained from Chmond Rd. (London) and used without further purification. The tanked oxygen was used and air was sparged with an air pump. The other reagents were analytical grade and all the solutions were prepared with double-distilled water.

1.2 Recommended procedure

5 mg of Co[P(TBPSOPP)] was added into a quartz double-layered reactor (self-designed) containing 35 ml of 3.74 mg/L MB solution, then stirred with 78HW-1 magnetic stirrer prior to irradiation with 450 W HPML. With air sparging, photocatalytic degradation took place in the reactor. Water was recycled in a 501 model thermostatic bath and the temperature of the reactor kept at 20°C except for the temperature experiments. The absorbance of the

sample solution were determined on model UV-754 spectrophotometer at 664 nm with glass cells (10 mm optical path length) every hour after standing for 5 minutes. Experiments performed under NSL were carried out in August and September in Lanzhou, Gansu, China (East longitude 103°53' and North latitude 36°03').

1.3 Calibration curve

A calibration curve was obtained for MB and found to be linear in the range of 0.75-7.5 mg/L. The MB concentrations and absorbances were well correlated with the regression equation as follows:

$$A=0.0139 +0.1439\times C \quad (R = 0.9979)$$

where A is the absorbance of the MB; C is the concentration of MB (mg/L) and R is the regression coefficient for the straight line.

2. RESULTS

2.1 The kinetics of photocatalytic degradation of MB solution

In the presence of Co[P(TBPSOPP)], the change of the visible spectra and the kinetics of photocatalysis of MB were investigated at pH 6.6. The contrast degradation curve of MB is shown in Fig. 1. From the relevant data, it can be seen that MB dramatically decrease with the increase of irradiation time. It was found that the logarithmic values of the concentrations of MB solution was presented in Fig.2 as a straight line with the increase of irradiation time. This indicates that the photocatalytic degradation of MB obeyed pseudo first-order kinetics. The rate equation can be represented as follows: $\ln C_t = \ln C_0 -kt$

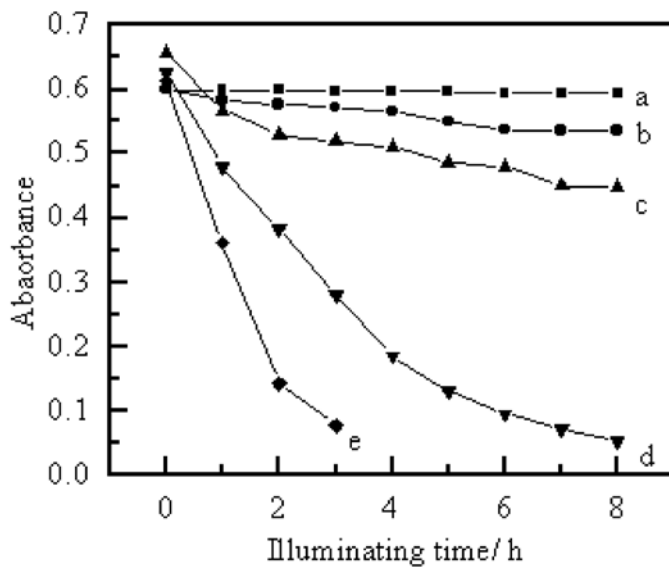


Fig.1 The degradation curves for various conditions

- a: No catalyst and in the dark;
- b: Absorption under 5mg catalyst and no illumination.
- c: No catalyst plus HPML;
- d: Absorption under 5 mg catalyst , HPML plus air pumping;
- e: Absorption under 5 mg catalyst, HPML, air pumping plus H₂O₂.

Compared with HPML, NSL had similar effect on the photocatalytic degradation of MB. The process also conformed the pseudo first-order kinetics.(Fig.2) The kinetics regression equations were shown below respectively:
 $\ln C_t = 1.5639 - 0.3544t$ (R = -0.9974), life time $t_{1/2} = 1.96$ h. (HPML)
 $\ln C_t = 1.4888 - 0.2598t$ (R = -0.9878), life time $t_{1/2} = 2.67$ h. (NSL)

From above, we can concluded that HPML has better effect than NSL because that HPML has fast degradation rate than NSL under the same conditions.

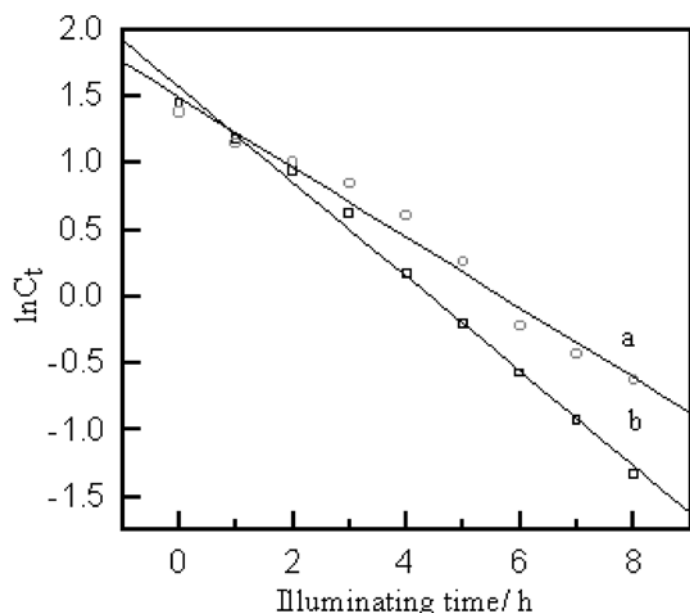


Fig.2 The kinetic curves with different light sources.
a: NSL; b: 450 W HPML.

2.2 Determination of COD

COD was determined according to the reported method^[11]. The contrast COD concentrations of working sample and measurement accuracy are listed in Table 1. It can be found that decreasing rate of COD, on the average, reached 47.2% after 8 hours photocatalytic degradation process. This may be due to the complete decomposition of MB.

Table 1 Measurement accuracy of COD and removal efficiency in photodegradation process.

	COD (mg/L)		confidence interval*	SD	Degradation ratio of COD
Before photocatalytic degradation	49.4	40.1	43.9±4.2	4.0	0
	44.2	41.9			
After photocatalytic degradation	27.1	22.2	23.2±3.3	3.1	47.2%
	23.8	19.7			

*Confidency level was 0.95.

2.3 Determination of decolourization rate

After 8 hours photocatalytic degradation, the solution of MB became colorless. The chromaticity and decolorization rates of the dyestuff in the aqueous solution were calculated according to the equations described previously^[12].

Eleven points were selected at 20 nm intervals to measure their absorbance in the visible spectrum band (420-620 nm). The decolourization rate and the relative chromaticity were determined from the absorbance of the sample solution and Pt-Co standard chromaticity under the selected eleven wavelengths.

The changes of chromaticity of MB in the sample solution are shown in Table 2. It is well known that MB can be bleached under NSL without any catalyst, however, from Table 2, it is just 29.6% of MB was self-bleached with the degradation rate of about 34.9%. In the presence of metalloporphyrin, though HPML has higher degradation rate than NSL, it was evident that the decolouring efficiency under the irradiation of NSL was much higher than HPML, presumably due to the excitation by stronger emission lines of NSL than HPML in the visual spectrum band.

Table 2 Data of chromaticity

	420	440	460	480	500	520	540	560	580	600	620	chromaticity
	0.272	0.215	0.250	0.217	0.156	0.093	0.047	0.020	0.009	0.005	0.003	500°

Pt-Co standard *												
initial sample	0.002	0.004	0.012	0.020	0.024	0.028	0.046	0.081	0.146	0.257	0.337	371°
ZSL self-sensitivity	0.011	0.013	0.016	0.022	0.026	0.030	0.035	0.053	0.096	0.149	0.221	261°
degraded sample	0.033	0.035	0.034	0.034	0.033	0.032	0.035	0.038	0.042	0.045	0.047	158°
NSL degradation	0.014	0.011	0.013	0.012	0.011	0.010	0.013	0.016	0.021	0.026	0.029	68°

*The absorbance of Pt-Co standard chromaticity was determined with a model 721 spectrophotometer [12].

2.4 Recovery of photocatalyst

The used photocatalyst was recovered and measured after twice reaction. It could be observed that photocatalytic activity of the catalyst reduced with the irradiation time. The activity of the recovered photocatalyst in the first recovery time was higher than the second time, which indicated that the photocatalyst obtained in the solution could be recovered to some extent for further photo-degradation.

3. DISCUSSION

3.1 The contrast disappearance of MB

Results of the photo-decomposition of MB in various conditions are presented in Fig. 1. It was shown that the concentrations of MB decreased with the increase of irradiation time. From curve (a) of Fig. 1 the absorbance did not vary at all and the slope is flat. It is well known that MB can be absorbed onto solid easily, but from curve (b), only a small amount of MB could be absorbed onto photocatalyst without irradiation. Only 10 per cent of MB could be photodegraded when illuminated with HPML in the absence of metalloporphyrin in curve (c), although MB have been used as a sensitizer in previous reports [13,14] for the photocatalytic degradation of organic contaminants in water. In curve (d), with added photocatalyst and illuminated with HPML, MB decreased rapidly and photocatalytically degraded completely within 8 hours with air sparging. The significantly greater slope was obtained for curve (e). The degradation rate greatly speeded up, and the decomposition of MB completely finished within 3 hours in the presence of 2.5×10^{-2} mol/L hydrogen peroxide.

3.2 Effect of pH

The effect of pH was studied in the pH range of 2.90-12.00 by adjusting pH with diluted sodium hydroxide or hydrochloride acid solution. The results shown in Fig. 3 indicate that the effect of pH on photocatalytic degradation rate was noticeable. The degradation rates of MB increase distinctly with the increase of the pH value.

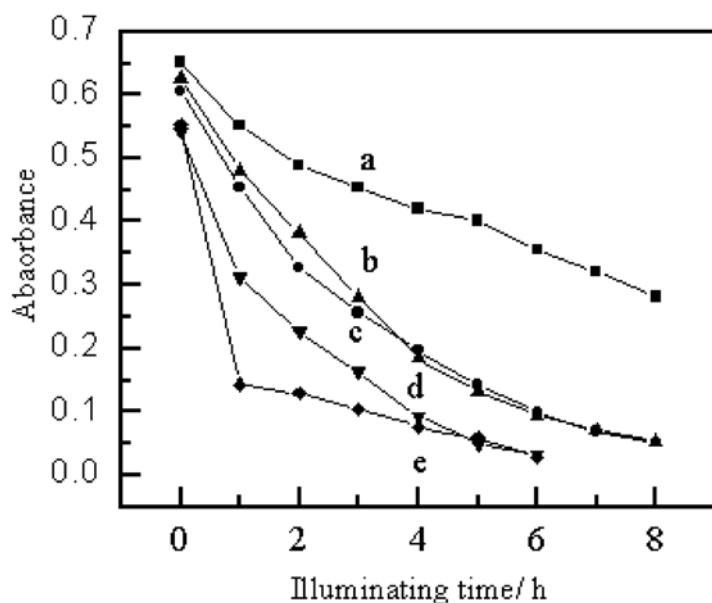


Fig.3 The pH effect on the degradation
a: pH 2.9; b: pH 4.2; c: pH 6.6; d: pH 9.3; e: pH 12.0.

3.3 Effect of working temperature

In order to analogize actual water supply, the temperatures of the photocatalytic degradation were measured from 293 to 313 K. Their kinetic parameters were shown in Table 3. It can be seen that the effect of temperature on the decomposition rates is not noticeable. Thus the working temperature of photocatalytic degradation should be chosen according to the temperature of ambient dye-containing water.

Table 3. The kinetic parameters of temperature effect

The temperature(K)	Kinetic equation	kinetic constant k (h ⁻¹)	Half time t _{1/2} (h)
293	lnCt=1.5644-0.3544t	0.3544	1.96
303	lnCt=1.3331-0.3591t	0.3591	1.93
313	lnCt=1.3576-0.3646t	0.3646	1.90

3.4 Effect of oxidants

During the course of photocatalytic degradation, the effects of various oxidants were measured. Their first-order kinetic curves are shown in Fig. 4. The effects of oxidants were significant when small concentration of oxidants were added. The HO· radicals play an important role in the catalytic oxidation reaction of dyes. The HO· was produced easily by the illumination of hydrogen peroxide [15,16], so the hydrogen peroxide was added to investigate its action. The MB was completely degraded in the presence of 2.5×10⁻² mol/L of hydrogen peroxide within 3 hours (curve c of Fig. 4), compared with 8 hours under air-saturated atmosphere (curve a) and oxygen-saturated atmosphere (curve b).

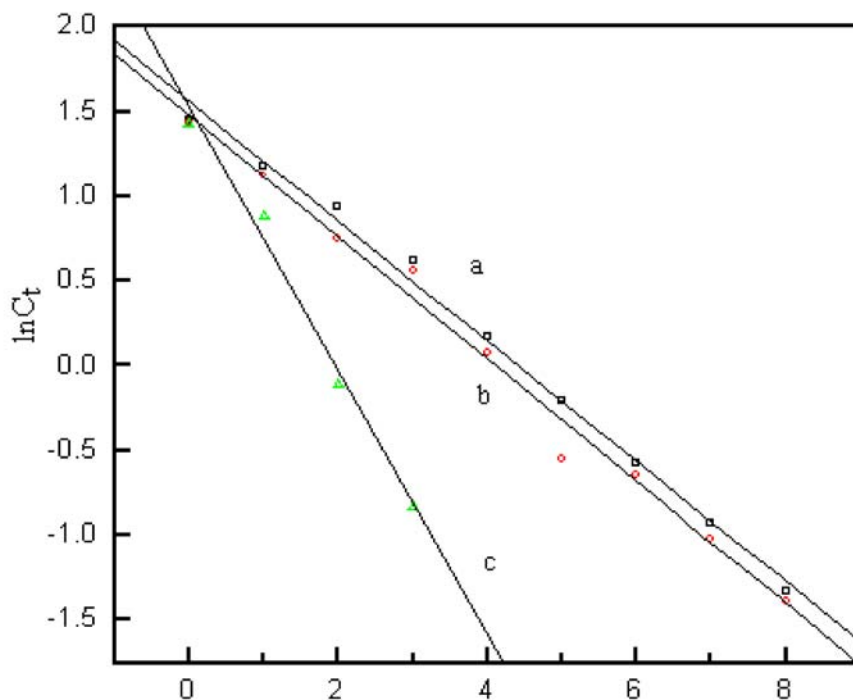


Fig.4 Kinetic curves with various oxidants
a: Air-Sparge; b: Oxygen-sparge; c: H₂O₂ plus air-sparge.

3.5 Effect of initial concentration of MB

According to the recommended procedure, the photocatalytic degradation was discussed by changing the initial concentration of MB solution from 2.05 to 6.75 mg/L. It was observed that initial concentration of MB has a significant effect on the degradation rate and it decreases with the increase of the initial concentration. The contrast

effect was shown for MB in Table 4. In this experiment, the optimum initial MB concentration of 4.25 mg/L was chosen to conduct the experiment.

Table 4 the kinetic parameters in various initial concentration of MB

Initial Concentration C_0 (mg/L)	6.658	5.442	4.253	2.085
The percentage of degradation	71.4%	80.6%	91.7%	86.6%
$\ln C_0$ (real value)	1.8345	1.7608	1.5638	0.7352
$\ln C_0$ (calculated value)	1.8950	1.6941	1.4480	0.7351
Decay kinetic constant k (h^{-1})	0.1713	0.2016	0.3544	0.4054
Half time $t_{1/2}$ (h)	4.91	3.44	1.96	1.71

3.6 Effect of amount of photocatalyst

In this procedure, 2, 5, 7 mg of metalloporphyrin were used respectively. The curves of photocatalytic degradation were also discussed. It is obvious that the amount of photocatalyst has a little effect on the degradation rate. Fast initial rate was obtained when more catalyst was added, but the same result was observed within 8 hrs.

3.7 Effect of different illuminants

It is well known that the emission spectra of HPML mainly focus on the ultraviolet band having the advantages of short-wave emission and large energy to initiate photochemistry reactions of chemicals. However, the spectrum of NSL is ranged from ultraviolet to near Infrared and with the main flux concentrated on the visible light band. In order to investigate the practical application of this technology in ambient water supply, NSL was chosen to use as the source of irradiation. It was found that for HPML, it is evident that the higher flux of illumination is, the larger photo-degradation rate is obtained. Compared with HPML, NSL had similar effect on MB. It can be concluded that this experiment could also be repeated with NSL. The potential usage of sun light in water treatment is indicated by these results.

4. CONCLUSION

MB aqueous solution can be degraded with irradiation with both HPML and NSL in the presence of Co[P(TBPSOPP)]. The degradation of MB in water obeys pseudo first-order reaction.

Photocatalyst can be deposited and recycled without second pollution.

After 8 hrs photocatalytic degradation, the dyestuff (MB) can be completely decolorized with the solution becoming colorless; the COD concentrations of dyestuff also dropped apparently.

The photocatalytic degradation of MB in water could be greatly accelerated in the presence of hydrogen peroxide.

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