Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(1):188-191
(http://derpharmachemica.com/archive.html)

Catalytic degradation of methyl orange under visible light by $(NH_4)_6[MnMo_9O_{32}]8H_2O$ with Waugh structure

Yuan Hua, Yang Fengzhen and Fan Xiaozhen

College of Chemistry and Chemical Engineering, Cangzhou Normal University, Cangzhou, Hebei, China

---

ABSTRACT

To study the catalytic degradation of methyl orange with Waugh Structure $(NH_4)_6$ $[MnMo_9O_{32}]$ $8H_2O$ as the catalyst under visible light. Results: different types of acid and different pH values have effect on the photocatalytic activity of Waugh Structure $(NH_4)_6$ $[MnMo_9O_{32}]$ $8H_2O$, catalyst quantity and initial concentration of methyl orange solution are important factors affecting the decolorization capacity of solution. Under visible light, 8 minutes decolorization capacity can reach 94.36% with the methyl orange solution at an initial concentration of 20mg / L, the heteropolyacid salt at a concentration of 0.3 g/L, and pH value adjusted to 2 with perchloric acid.

Key words: Waugh Structure, $(NH_4)_6[MnMo_9O_{32}]8H_2O$, catalytic degradation

---

INTRODUCTION

Sewage contains large amounts of azo organic pollutants, with high biological toxic, which are difficult to degrade themselves in natural waters, the polluted water for irrigation of crops into the animal occurs reductive decomposition, and produces carcinogenic aromatic amine compounds, which pose threat to the health of humans and other biology. In recent years, novel green catalyst [1] - heteropoly compounds have been attracted more and more attention by catalyst workers, due to its merits of excellent photocatalytic degradation, chemical stability, mild reaction conditions, easy to regenerate, while has both acidic and redox properties, no corrosion of equipment and the environment etc. Methyl orange is a representative of the azo compound, there were reports of Keggin type of phosphorus tungstate have good photocatalytic activity to Methyl Orange [2-4], catalysis studies on Waugh heteropoly anion is still in infancy. In this paper, the catalytic degradation on methyl orange was studied, and took methyl orange solution as the target degradation, Waugh Structure $(NH_4)_6[MnMo_9O_{32}]8H_2O$ as a catalyst.

MATERIALS AND METHODS

1.1Instrument and Reagents
760CRT UV-Vis spectrophotometer (Shanghai Precision Scientific Instruments Inc.), pHS-3C pH meter (Shanghai Kang Instrument Co., Ltd.)

Methyl orange (Shanghai SSS Reagent Co., Ltd. AR); Perchloric acid (Tianjin Dongfang Chemical Plant, AR);

1.2Test method
1.2.1 Synthesis of $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$
To synthesize orange-red crystals Waugh Structure $(NH_4)_6[MnMo_9O_{32}]8H_2O$ according to the method in literature[5]

1.2.2 Light-catalyzed Reaction
Place a certain concentration of methyl orange solution and the catalyst solution into a beaker, adjust the pH to 1 ~ 4

with perchloric acid solution [6], use 40 W fluorescent to simulate a visible light source, the light source distance is 200 cm, place it on a magnetic and stir with intermediate speed stirring, every 1 minute to take a sample, and measure the absorbance at a certain wavelength.

1.2.3 Analytical Method
Firstly use UV-Vis spectrophotometer to scan methyl orange solution under full-wave band of ultraviolet and visible regions, to determine the maximum absorption wavelength of methyl orange at 463 nm, and scan Waugh Structure $(NH_4)_6[MnMo_9O_{32}]8H_2O$ under full-wave band, to determine the maximum absorption wavelength of 227 nm having a strong absorption in the ultraviolet region, the visible region has a weak absorption at 490 nm, both have non-interference in the visible region, it is determined to measure the absorbance of sample at 463 nm.

For degradation effect uses Decolorization Capacity (DC) of sample to compare, calculation formula for decolorization capacity is as followed:

$DC = [(A_0 - A_t) / A_0] \times 100\%$,

A_0: Absorbance of the sample before light,
A_t: Absorbance of the sample at the time of t under the light.

1.3 Results and Discussion
1.3.1 Photocatalytic activity of methyl orange
Test the degradation situation of Blank methyl orange acid solution under the condition of acid solution or only under condition of light, or under combined conditions, there was almost no activity for methyl orange in short time, but when added certain quantity of acid $(NH_4)_6[MnMo_9O_{32}]8H_2O$ to the methyl orange solution, it was quickly degraded to show photocatalytic activity of the catalyst.

1.3.2 Selection of media Acid
Respectively use nitric acid, sulfuric acid, hydrochloric acid, and perchloric acid to adjust the pH of the solution of methyl orange to 2, without catalyst, and under the light, every ten minutes to take sample and measure the absorbance, see Table 1.

Tabel 1 Absorbance Results by adjusted with different acids

	Absorbance			
Time（min）	HNO_3	HCl	H_2SO_4	$HClO_4$
0	1.273	1.265	1.220	1.356
10	1.318	1.289	1.247	1.357
20	1.305	1.287	1.243	1.356
30	1.009	1.284	1.238	1.355

The results showed that: under the effect of several medium acids lighting for 30 minutes, the solution had varying degrees of change in absorbance. The smallest change in absorbance of 0.002 was the acid methyl orange solution adjusted by perchloric acid, and degradation of the other three catalytic acid to methyl orange were higher than that of perchloric acid, so chose perchloric acid as media acid for its no degradation to methyl orange solution.

1.3.2 Absorbance change of methyl orange in UV-visible spectra at different reaction times
Take 100 mL of 10 mg / L of methyl orange solution, adjust pH to 2 with $HClO_4$ solution, add a certain amount of catalyst. It was found that: As the reaction proceeding, the absorbance of methyl orange solution rapidly declined, eight minutes later, the main wavelength of absorption was almost zero, indicating that the photocatalytic degradation to methyl orange was with high reactivity and no other peaks was generated.

1.3.3 The effect of amount of catalyst on photocatalytic decolorization capacity
Maintain the initial concentration of methyl orange solution at 10 mg / L, adjust pH to 2 with $HClO_4$ solution, respectively add different amounts of catalyst, light for eight minutes, measure the absorbance before and after the light, thereby the photocatalytic decolorization capacity were obtained in Table 2

Table 2 Effect of amount of catalyst on photocatalytic decolorization capacity

Catalys amount (g/L)	0.1	0.3	0.5	0.7
DC(%)	88.72	92.03	90.90	89.92

It can be seen from Table 2: when the amount of Catalyst at 0.3g / L, the decolorization capacity was maximized. When increasing the concentration, and light scattering, the photocatalytic reaction capacity reduced, thus it was determined the optimum amount of catalyst was 0.3g / L.

1.3.4 Effect of different initial concentration of methyl orange on decolorization capacity
Respectively prepare 5, 10, 15, 20, 25 and 30mg / L of methyl orange solution, adjust pH to 2 with $HClO_4$ solution, keep the catalyst at 0.3g / L, and conduct photocatalytic degradation reaction for 8 minutes, the experimental results were shown in Figure 1.

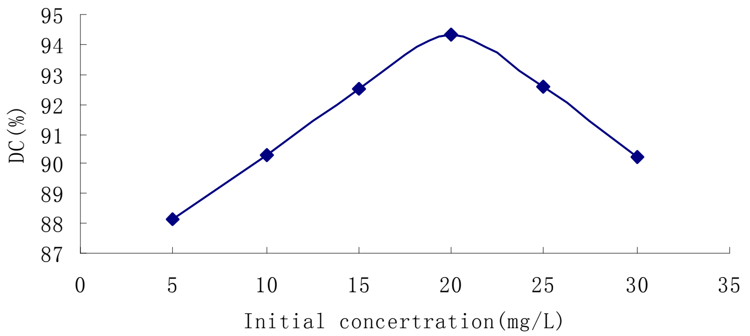

Figure 1 Effect of different initial concentration of methyl orange on decolorization capacity

It can be seen from Figure 1, with elevated concentrations of methyl orange solution, decolorization capacity first increased then reduced. When the concentration was 20mg / L, the decolorization capacity was maximum, which was due to with concentration of methyl orange increased the color degree also increased, translucent solution deteriorated, the photocatalytic activity decreased, resulting in methyl orange decolorization declined, so choose the initial concentration of 20 mg/L of methyl orange solution as the best.

1.3.5 Effect of Acidity of methyl orange on decolorization capacity
Maintain initial concentration of methyl orange solution at 20mg / L, the catalyst concentration at 0.3g / L, adjust pH at different acidity with $HClO_4$, light for eight minutes, take the solution every minute and measure the absorbance, the results were shown in Figure 2

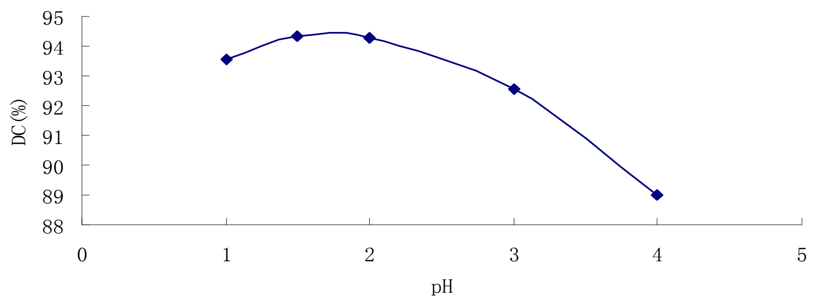

Figure 2 Effect of Acidity of methyl orange on decolorization capacity

It can be seen from Figure 2: with the pH of methyl orange increase, it showed a trend of first increasing then declining for decolorization capacity, when pH at 1.5 to 2, decolorization capacity of methyl orange was maximum, taking into account the acidity increasing, not only equipment corrosion increased, and the post-acid treatment neutralized with alkali increased, with consideration of overall economic efficiency and the protection of equipment, select optimum pH for photocatalytic degradation of methyl orange at 2.

1.3.6 Kinetics study of methyl orange solution photocatalytic degradation
Under 40 W visible light, the concentration of methyl orange solution was within 0 ~ 30mg / L, the concentration and absorbance have a good linear relationship, C = 26.124A-0.376, correlation coefficient r = 0.9999. Kept concentration of methyl orange solution at 20 mg / L, the catalyst concentration 0.3g / L, adjusted pH to 2 with $HClO_4$ solution, with lamp visible light, measured the absorbance of the sample solution at different times, and conduce regression analysis for In (Co / Ct) and light degradation time t, linear equation y = 0.425x + 1.2108, R = 0.9987, showed that Waugh structure $(NH_4)_6[MnMo_9O_{32}]8H_2O$ photocatalytic degradation of methyl orange was first-order kinetics, under these conditions. The apparent reaction rate constant K was 0.425, the half-life $t_{1/2}$ was 1.63 min.

CONCLUSION

Under visible light, this experiment, taken Waugh Structure $(NH_4)_6[MnMo_9O_{32}]8H_2O$ as a catalyst, for catalytic degradation of methyl orange were studied. The results showed that: initial pH value and adjust the pH value with different acids to Waugh structure $(NH_4)_6[MnMo_9O_{32}]8H_2O$, photocatalytic activity of influential catalyst amount and initial concentration of methyl orange solution were important factors for affecting decolorization capacity. The optimum reaction conditions of visible light, pH to 2 adjusted with perchloric acid solution, the concentration of solution $(NH_4)_6[MnMo_9O_{32}]8H_2O$ at 0.3 g/L, the initial concentration of methyl orange solution at 20 mg/L, decolorization capacity could reach 94.36% in 8 minutes, the photocatalytic degradation of methyl orange was as first-order kinetics reaction.

Acknowledgement
The project was financially Supported by the science and technology project of Hebei Province
15213617

REFERENCES

[1] Wang Enbo, Hu Changwen, Xu Lin. Introduction to Multi-acid Chemistry [M]. Beijing: Chemical Industry Press,**1998**: 29-33.
[2]Zhu Xiuhua,Wang wei,Li Haicheng. *Shanghai Environmental Sciences*, **2001**,20(9):444-447.
[3]Gou Hua,Luo Suxing,He Xiaoying,et al. *Journal of Anhui Agri. Sci*. **2008**, 36(1) : 89- 90, 101.
[4]Yang Shuijin,Zhang Yijun,Zhang Haili. *Chemical Reaction Engineering and Technology*, **2011**,27(6):562-566.
[5] Huo Guoyan, Yuan Hua, Liu Wei et al. *Journal of Hebei University. Natural Science Edition*, **2002**,22(1):19-22.
[6] Yuan Hua, Wang Lixia, Liu Wei et al. *Journal of Hebei Normal University*: Natural Science Edition, **2007**,31 (supplemented): 178-180.