Effect of Humic Acid on the Degradation of Methylene Blue by Peroxymonosulfate

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Abstract: Methylene blue dye has been widely used in many industries and usually released in natural water sources, which become a health threat to human-beings and microbes. This paper demonstrates an oxidation method to remove methylene blue in water. The effect of natural organic matter humic acid, on the degradation of methylene blue using PMS was investigated. The results show that PMS could effectively degrade 50 mg/L methylene blue (>95%) when the PMS concentration was larger than 1.0 mM. Humic acid had either negative or positive impact on the degradation processes because of the co-existence of several competitive degradation mechanisms (I: humic acid competes with methylene blue for PMS; II: humic acid activates PMS to produce sulfate radicals; III: Cl⁻ competes with methylene blue for sulfate radicals). This study is expected to provide valuable information to improve in situ remediation of dye-contaminated wastewater in the existence of natural organic matters.

Keywords: Humic acid; Peroxymonosulfate; Methylene blue; Degradation.

1 Introduction

The control of water quality is of paramount importance to both environment and human health [1,2]. Thousands of pollutants can be found in wastewater, such as heavy metals, phenols, polychlorinated biphenyls, pesticides, and dyes [3-5]. It is reported that 10-15% of dyes are lost in the effluent process. Among these, organic dyes are highly colored, harmful to human beings, and result in significant increase of COD in water bodies [6]. Methylene blue is a cationic dye and widely used by industries including textile, printing, dye manufacturing, plastics, pharmaceutical, and photography industries. Its complicated chemical structure causes its recalcitrance to conventional biological treatment.

Chemical remediation has been widely applied for wastewater treatments due to its high efficiency for most pollutants and easy industrialized operation, among which, advanced oxidation process (AOP) based on peroxymonosulfate (PMS) or persulfate is a highly efficient method for a wide range of pollutants, such as phenol, dyes, and polychlorinated biphenyls [7-9]. Peroxymonosulfate is a strong oxidant with the standard potential of 1.82-2.01V. Transition metals, heat, radio-activation, alkali, and carbon based materials have been applied to activate PMS to produce sulfate radicals to promote the oxidation reaction [10-13]. However, the introduction of synthetic chemicals or metals into the system may lead to the operation difficulty or secondary pollution risk. The use of heat and radio-activation is complicated and difficult for large-scale operation. Previous studies also implied that the organic compounds such as ketones, primary alcohols, and low carbon chain aldehydes could activate PMS or persulfate for chemical oxidation applications in the field scale [14]. These organic compounds exist broadly in the natural water or soil. They are environmental friendly and derived from natural resources. In this research, the effect of humic acid which is a natural organic matter, on the methylene blue degradation using PMS was investigated for the first time.

This paper addresses an in-situ oxidative wastewater remediation method to degrade methylene blue using PMS in the absence of any activator and in the addition of a nature organic matter humic acid. The effect of humic...
acid on the degradation of the methylene blue effluent under different concentration of PMS was studied. We also conducted a list of experiments to elucidate the methylene blue degradation mechanism with the coexistence of humic acid and PMS. It is expected that this study could give some insights on how natural organic matters affect in situ oxidative remediation process of polluted natural water.

2 Materials and Methods

2.1 Chemicals and Materials

Methylene blue, humic acid, peroxymonosulfate, sodium hydrogen, sulfuric acid, ethanol, and sodium chloride were purchased from Sigma Aldrich and used as received. Deionized water from Milli-Q (Millipore) with resistivity >18.2 MΩ·cm was used in all the experiments.

2.2 Experimental procedures and analysis

The batch experiments were conducted at room temperature (24°C). Different dosages of humic acid and PMS were added into wastewater that contained methylene blue, in a 50 mL tube. The pH value was adjusted to the desired level by adding either 0.1 M sulfuric acid or sodium hydroxide. Then the oxidative reaction was conducted on a reciprocating shaker with the shaking speed of 50 rpm under dark. At selected time intervals, about 10 mL of samples was taken out from the tube for analysis, and scavenger (0.1 mL ethanol) was added into the sample immediately. The samples were placed inside a UV-VIS spectrophotometer cell (Thermo Scientific Evolution 60S) to determine the maximum absorption wavelength of 660 nm. The dye removal efficiency (%) was expressed as follows: $C_0 - C$ / $C_0$, in which, $C_0$ was the initial concentration of methylene blue, and $C$ was final concentration of methylene blue after the reaction. The final pH values of the solutions were measured by the pH metro (Thermo Fisher Scientific). All the experiments were repeated three times and the degradation efficiency was the average of three measurements with the relative errors less than 5%.

Ethical approval: The conducted research is not related to either human or animals use.

Figure 1: The effect of pH on the degradation of 50 mg/L methylene blue using 1.0 mM PMS and at different reaction time.

3 Results and Discussion

3.1 Degradation of methylene blue by PMS at different pH value

The peroxymonosulfate (PMS) is a strong acidic oxidant due to the existing of HSO$_3^-$, which could oxidize methylene blue without the aid of any activator. Figure 1 shows the effects of solution pH values (2.3 to 9.0) and reaction time on the degradation of methylene blue. In the first half hour, concentration of methylene blue decreased from 50 mg/L to about 20 mg/L for all the pH values except pH of 9.0. After 24 h reaction, the methylene blue was significantly degraded (approximately 85% ~ 90% efficiency) for all conditions. And for the same pH sample, with the increase of reaction time, the methylene blue degradation efficiency enhanced accordingly. Obviously, reaction time but not the initial pH value greatly affects the degradation efficiency of methylene blue.

Another interesting phenomenon is that the dye degradation efficiency was much lower at pH 9 at a reaction time of 1.5 h. This result agreed well with previous study [15], and it can be explained by self-decomposition of PMS in alkaline conditions. At reaction time of 5 h and 24 h, the degradation efficiency was significantly improved for all pH values, and the final pH was found to be 3. Which indicated that in these runs the decomposition of methylene blue could decrease the pH values, resulting in the impedance of the self-decomposition of PMS.

It is believed that the relatively high concentration of PMS (1.0 mM) may hidden the effect of the pH value at a low loading of methylene blue. Therefore, the effect of the pH on the degradation of methylene blue at a relatively low concentration of PMS (0.5 mM) was further investigated. As shown in Figure 2, the degradation efficiency shows a similar trend as that using 1.0 mM PMS. But all the
methylene blue degradation efficiencies were less than 60%. As shown in Figure 1 and 2, the pH value has slight impact on the degradation efficiency when the pH value was lower than 7, but the degradation efficiency decreased significantly, when the pH value was larger than 7. This indicates that the self-decomposition of PMS was not negligible at a low concentration of PMS. Since extremely low or high pH is very rare in the natural wastewater system, it can be concluded that the effect of pH was negligible in this methylene blue degradation process. In the following study, the pH values were adjusted to 7.0 ± 0.2 to mimic the natural water and remain high degradation efficiencies.

The degradation rate constant ($k_{obs}$) based on the pseudo first order model was less than 0.1 min$^{-1}$ calculated from the data (see Figure 1 which was much less than those previously reported in literatures. As demonstrated in Ghauch's study, the degradation rate constant of methylene blue in a heated persulfate process was 4.81-9.05 min$^{-1}$ at a pH range of 4 - 9 [16]. The distinctive difference in the reaction rate can be attributed to the absence of activators in this study. However, from the view of in situ remediation and environmental benefits, oxidation without additional chemicals should be a better choice.

### 3.2 Effect of the PMS concentration on the degradation of methylene blue

Figure 3 demonstrates the degradation effects of methylene blue with a concentration ranging from 50 mg/L to 200 mg/L under different PMS concentrations. The methylene blue degradation efficiency was increased with the enhancement of the PMS concentration in all the designed experiments. However, the degradation curve followed a slightly different trend depending on its initial concentration. A low dosage of PMS (0.5 mM) could not effectively degrade methylene blue at a relatively high concentration (larger than 50 mg/L). When the PMS concentration was increased from 1.0 mM to 2.5 mM, the degradation efficiency of 100, 150, and 200 mg/L methylene blue was increased to 28%, 47%, and 50%, respectively. In the addition of 6 mM PMS, the degradation efficiency for 150 and 200 mg/L methylene blue was 88% and 77%, respectively. At a high concentration of methylene blue (150 mg/L or 200 mg/L), the degradation efficiency was not significantly improved even in the addition of high concentration of PMS (6.0 mM in comparison with 3.5 mM PMS). This phenomenon could be attributed to the competitive consuming of PMS by intermediates [17,18].

### 3.3 Effect of humic acid

Humic acids occur in the natural water with the concentration ranging from 0.1~20 mg/L [19]. According to the previous studies, humic acid was one of the water pollutants that had impact on the water purification process due to its chelating properties [20,21]. Recently, Fang et al. reported that the redox active moiety of quinone in humic acid could act as an effective catalyst to activate persulfate to degrade polychlorinated biphenyls [22]. It is unclear whether humic acid activates PMS to produce sulfate radicals, which is possible to accelerate the degradation of methylene blue. Therefore, Herein, the effect of humic acid on degradation of methylene blue in the existence of PMS and its degradation mechanism was elucidated.
3.3.1 Effect of humic acid at different PMS concentrations

Based on our aforementioned results, the degradation efficiency of methylene blue was < 70% at a concentration of PMS < 2 mM and methylene blue ≥ 100 mg/L. Figure 4a shows the effects of different amount of humic acids (0, 2, 5, 10, 15 mg/L) on the degradation of methylene blue with the mole ratio of PMS to methylene blue of 3.2. When the concentration of humic acid was less than 2 mg/L, its effect on the degradation efficiency was negligible for all the designed methylene blue solutions. In a 50 mg/L methylene blue solution, the addition of 5 mg/L humic acid accelerated the degradation efficiency (from 31% to 60%). In a 100 mg/L methylene blue with 1mM PMS, the addition of 10 or 15 mg/L humic acid increased the degradation efficiency from initial 54% to more than 64%. The results shown in Figure 4b implies that 30 mg/L humic acid was beneficial for the degradation of 150 mg/L methylene blue (approximately 60% degradation efficiency, in comparison with that in the absence of humic acid 40%). In a 200 mg/L methylene blue effluent with 6 mM PMS, 35 mg/L humic acid could achieve the maximum degradation efficiency (95%), that was also greater than that in the absence of humic acid. It was noticeable that sometimes the addition of humic acid had the negative effect on the methylene blue degradation as shown in Figure 4b.

3.3.2 Effect of humic acid on the methylene blue degradation under a relatively high concentration of PMS

Figure 5 presents the effect of humic acid on the degradation of methylene blue when the PMS concentration was relative high. More than 95% degradation efficiency was achieved in a 50 mg/L methylene blue effluent when the PMS was 2 mM for all the examined humic acid concentrations. The degradation efficiency was higher than 93% for 100 mg/L methylene blue with a 5 mM PMS. The increase of the humic acid concentration (0 to 30 mg/L) could slightly reduce the degradation efficiency. It could be explained by the competitive consuming of PMS by humic acid.

3.3.3 The degradation mechanism of methylene blue with the coexistence of PMS and humic acid

The aforementioned results demonstrate that humic acids had either positive or slightly negative effects on the degradation efficiency of methylene blue. The mechanism behind these effects is likely related to the competitive consumption of PMS between humic acid and methylene blue, as well as the specific roles of humic acid in facilitating or inhibiting the degradation processes.

Figure 4 a & b: The effect of humic acid on the degradation of methylene blue using different PMS concentrations for 24 h.

Figure 5: The effect of humic acid on the degradation of 50 mg/L and 100 mg/L methylene blue at high concentration of PMS (the mole ratio >12.8) for 24 h.
degradation of methylene blue. The negative effect may be attributed to the competitive reaction between humic acid and methylene blue with PMS, which was previously reported [23,24] and this was in accordance with the results obtained in this study (see Figure 1S).

Results shown in Figure 4 demonstrate that in a low loading of PMS and humic acid could accelerate the degradation of methylene blue. This result indicates that humic acid may act as the activator to promote the generation of free radicals from PMS. In order to elucidate the effect of humic acid on free radical generation, a radical quenching experiment was conducted. Ethanol, whose rate constant with sulfate radical is $1.6-7.7 \times 10^7 \text{M}^{-1}\text{S}^{-1}$ [25] was selected as the scavenger. Figure 6 compares the degradation efficiency of 50 mg/L methylene blue using 0.5 mM PMS in the absence and presence of humic acid and ethanol. The results illustrate that, only the addition of 5 mg/L humic acid increased the degradation of methylene blue from 39.3% to 62.8%, indicating that humic acid could greatly accelerate the methylene blue degradation. When ethanol was added, the degradation efficiency decreased significantly. Similar trend was observed in 100 mg/L methylene blue solution with the addition of 10 mg/L humic acid and 100 mM ethanol. Therefore, we can conclude that humic acid is an effective activator to initiate sulfate radicals to degrade methylene blue at a low loading of PMS, and this result agreed well with previous research [26]. Besides, methylene blue ($C_{16}H_{18}N_3ClS$) is a cationic dye, with Cl$^-$ counter anion that is formed during its dissolving process. Previous research reported that sulfate radicals could be consumed by Cl$^-$ [27]. As shown in Figure 6, when 150 mM NaCl was added to the effluent, the degradation efficiency was decreased from 62.8% to 44.3%, proving that Cl$^-$ inhibited the methylene blue degradation process.

Based on these results, a degradation mechanism was proposed and described in Figure S2. Humic acid acts as the natural activator for PMS to produce sulfate radicals, which could promote the degradation efficiency of methylene blue. Meanwhile, both humic acid and methylene blue competitively react with PMS, resulting in a negative impact of humic acid on the methylene blue degradation. In addition, the Cl$^-$ from methylene blue acts as the radical scavenger to reduce the methylene blue degradation efficiency as well.

4 Conclusions

This paper addresses a method to degrade methylene blue in effluents using peroxymonosulfate (PMS) without the usage of any additional activator. The results demonstrate that the PMS was capable of degrading methylene blue effectively without any other activator and at a relatively high PMS concentration. In a low PMS concentration (0.5 mM PMS VS. 50 mg/L methylene blue), the methylene blue degradation efficiency was significantly decreased and extremely low degradation efficiency was observed when the pH was greater than 7. Humic acid could activate the PMS to produce sulfate radicals to promote the methylene blue degradation. However, the degradation efficiency could be reduced by the competing reactions between humic acid and methylene blue with PMS when the PMS is at a high dosage. Other elements (e.g. Cl$^-$) in the natural water may also act as the radical scavenger for sulfate radicals and resulted in the reduction of the degradation efficiency. All these reactions synergically occurred in methylene blue effluent system and led to a complicated degradation mechanism. It is expected that this research can provide some insights to efficiently control the degradation of methylene blue in wastewater using low cost PMS as the oxidizer.

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