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# Rapid and simple spectrophotometric determination of persulfate in water by microwave assisted decolorization of Methylene Blue

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ABSTRACT

A rapid and simple method for determination of persulfate in aqueous solution was developed. The method is based on the rapid reaction of persulfate with Methylene Blue (MB) via domestic microwave activation, which can promote the activation of persulfate and decolorize MB quickly. The depletion of MB at 644 nm (the maximum absorption wavelength of MB) is in proportion to the increasing concentration of persulfate in aqueous solution. Linear calibration curve was obtained in the range 0–1.5 mmol/L, with a limit of detection of 0.0028 mmol/L. The reaction time is rapid (within 60 sec), which is much shorter than that used for conventional methods. Compared with existing analytical methods, it need not any additives, especially colorful $Fe^{2+}$, and need not any pretreatment for samples, such as pH adjustment.



## Introduction

In recent years, persulfate has been attracted increasing attention as a stable and powerful oxidant. Persulfate is always applied for degradation of organic contaminants in groundwater and wastewater (Fang and Shang, 2012; Yuan et al., 2013; Ji et al., 2014). Though persulfate has a redox potential of $E^0$ = 2.01 V (Amin, 1981), activation is necessary for application because of its low reactivity (Yang et al., 2009). A more powerful sulfate radical ($SO_4^{\cdot-}$) with $E^0$ = 2.6 V can be produced by activation via thermal method (Huang et al., 2002), UV (Hori et al., 2005), metal ions (especially $Fe^{2+}$) (Liang et al., 2004) and activated carbon (Zhang et al., 2013). Microwave (MW) (Yang et al., 2009) is also an attractive thermal method to activate persulfate. Yang et al. (2009) discovered that, with MW process, persulfate can oxidize azo dye Acid Orange 7, and the decolorization reached to 100% in 5 min, compared with a few hours without activation.

Despite that persulfate has a versatile application in many aspects, there are only several methods for determination of it. Wahba et al. (1959) studied the stoichiometric relationship between the redox reaction, then reported the reductometric titration method. Amin (1981) proposed the polarography method which was based on the various changes in current polarography with different concentrations of persulfate. Until lately, Liang et al. (2008) investigated the relationship between the concentrations of persulfate and the absorbance changes of the solution, and developed the

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spectrophotometric method. Among these methods, the most common ones were based on Eq. (1).

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2 \quad (1)$$

The traditional titration method, which was simple and accurate, involved a back-titration by thiosulfate. Together with the slow rate between persulfate and iodide, the reaction time was lasting over 40 min (Huang et al., 2002). Liang et al. (2008) created the rapid spectrophotometric method and reduced the reaction time to 15 min via $Fe^{2+}$ activation. But the process needs pretreatment of sample, such as adjustment of the pH in solution, and needs adding colorful $Fe^{2+}$ into the system, which may disturb the spectrophotometric determination. On the other hand, these determination methods of persulfate always focus on the concentration larger than 1 mmol/L (Wahba et al., 1959; Liang et al., 2008). Considering the numerous applications of persulfate, it is very necessary to develop a sensitive method for determining the lower concentration of persulfate in aqueous solution.

Dyes, which can be decolorized by strong oxidants, were used as indicators (Jurado et al., 2006; Dhaouadi et al., 2006). Zou et al. (2014) reported a spectrophotometric method of peroxymonosulfate by measuring the decolorization extent of Methylene Orange via $SO_4^{\cdot-}$ (Eq. (2)), which was produced by $Co^{2+}$-activated peroxymonosulfate. Ding et al. (2011) proposed a new method which was used to determine the concentration of persulfate by means of decolorization extent of four dyes. In case of the slow reaction rate of persulfate, Ding et al. (2011) combined normal heating with $Fe^{2+}$ activation methods for acceleration. As a result, it can be completed in a few minutes. However, it may lead some obstructions to the scale application. First, as the traditional method, it needs to adjust the pH of sample. What's more, both thermal activation and metal iron activation were used, which made the system complicated and tedious.

$$\text{Dye} + SO_4^{-\bullet} \rightarrow \text{Decolorized dye} + SO_4^{2-} \quad (2)$$

In this article, we developed a new method to determine persulfate in aqueous solution by measuring the decolorization extent of Methylene Blue (MB) via microwave (MW) process. It was found that a method with more rapid, convenient, and simple procedures was achieved. Under the optimized conditions, a good linear correlation was shown between the decolorization extent and the persulfate concentration. To check the feasibility and accuracy of the proposed method, we also make a comparison between our proposed method and the classic iodometric spectrophotometric methods.

## 1. Materials and methods

### 1.1. Reagents and solutions

All the used chemicals were of analytical reagent grade. Sodium persulfate, potassium iodide, sodium hydroxide and hydrochloric acid were purchased from Shanghai Chemical Reagent Company, China. MB was purchased from Tianjin Kermel Chemical Reagent Company, China. Solutions of 1.0 mol/L $H_2SO_4$ and 1.0 mol/L NaOH were used to adjust pH. All experiments were carried out using double distilled water.

### 1.2. Apparatus and measurement procedure

The decolorization experiments were conducted in a series of polypropylene ethylene plastic pipes (10.0 mL) with a total reaction solution volume of 5.0 mL. Sample solutions of persulfate (1.0 mL) and MB (4.0 mL) were mixed. The mixture solution was placed in an oven for a specific time as required. Unless otherwise specified, the initial concentration of MB was 10 mg/L, and the reaction time was 60 sec. MW radiation was provided by a domestic MW oven (900 W). After this process, the pipes were quickly transferred into a water bath for cooling down to room temperature (20 ± 1°C). It was worth to mention that, during such a short period of time, the loss of the solution caused by volatilization was negligible. The UV–vis absorbance of samples was analyzed with a Shimadzu UV1206 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). The degradation of MB was monitored by measuring the maximum absorbance at $\lambda$ = 664 nm. The decolorization extent was characterized by $\Delta A$, $\Delta A = A_0 - A_t$, where $A_0$ and $A_t$ were the absorbance of the dye solutions before reaction and after MW process of time t. The changes in pH of the mixed solution of persulfate and MB during the MW process were also investigated. $\Delta$pH was the difference in pH before and after MW process. To ensure the accuracy and replicability of the collected data, the experiments were operated at least three times under identical conditions.

## 2. Results and discussion

### 2.1. Effect of reaction time

MB, one of the basic dyes, was used as the indicator for the determination of persulfate. MW activation, rather than $Fe^{2+}$ activation, was used to promote the reaction. The influence of MW reaction time on the decolorization extent of MB was investigated and the results are shown in Fig. 1. It shows that for various concentrations of persulfate, all the reactions took

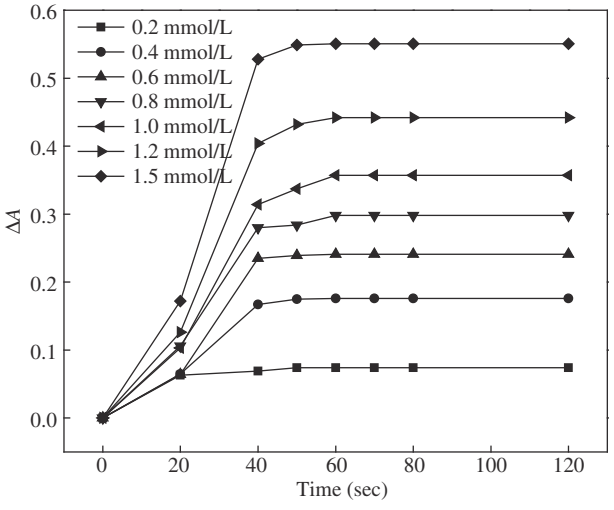


**Fig. 1 – Effect of reaction time on the decolorization of Methylene Blue (MB) by persulfate with various concentrations under microwave (MW) process.**