마이크로웨이브를 이용한 메틸렌 블루의 펜톤산화

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Microwave-assisted Fenton degradation of methylene blue

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Abstract

This work experimentally determined the effect of combining of microwave irradiation and the Fenton process on decolorization of methylene blue ($C_{16}H_{18}N_3SCl$, MB). As [H_2O_2] increased from 2.65 to 4.41 mM, the decolorization of MB increased from 22.7 to 99.1%. As [Fe^{2+}] increased from 0.07 to 0.18 mM, the decolorization of MB increased from 24.0 to 98.5%. MB removal efficiencies were $\geq$ 95% at [H_2O_2] $\geq$ 3.5 mM and 3.5 $\leq$ [H_2O_2]/[Fe^{2+}] $\leq$ 17.3, but [H_2O_2]/[Fe^{2+}] $\geq$ 20 caused a decrease in MB removal. A two-stage kinetic model matched the experimental data well.

Keywords: Fe^{2+}, Fenton, H_2O_2, Kinetics, Microwave, Recalcitrant wastewater

1. Introduction

Dyeing wastewater is discharged by many industries and is a serious environmental contaminant because the dyes are designed to resist chemical and biological degradation[1, 2]. Without proper treatment, release of this wastewater can cause ecological damage and threaten human health[2].

H_2O_2 is commonly used as an oxidant because its degradation products are environmentally benign. Activation of H_2O_2 by transition-metal ions for degradation of organic dyes has been explored actively[1, 3, 4]. The most widely-used process is the homogeneous Fenton reaction (Fe^{2+}/H_2O_2), in which the organic pollutants are degraded by reactive oxygen species such as hydroxyl radical ($OH^{\cdot}$)[1, 3]. The Fenton reaction can remove significant proportion of recalcitrant and toxic organic compounds, and can increase the biodegradability of organic compounds [5]. Due to high oxidation potential of $OH^{\cdot}$ (E^0=2.8V), it is capable of oxidizing a great variety of organic compounds or mineralizing them to CO_2 and H_2O. The major disadvantage is the long time needed to obtain good efficiencies (in general $\geq$ 30min)[6]. Methods to reduce the time required to degrade micropollutants would be useful.

Microwave heating has been used to promote oxidative degradation of biorefractory wastewaters due to its advantages of speed, high efficiency, and non-polluting attributes[4, 7]. Microwaves (300 MHz $\leq$ frequency $\leq$ 300 GHz) provide the advantages of uniform and rapid heating. Microwaves also have nonthermal effects (e.g., promoting vibration of chemical bonds, decreasing activation energies, and increasing reaction rates[4, 6]) that may excite reactant molecules to higher vibrational and rotational energy levels[4]. Although microwaves

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can produce homogeneous and quick thermal reactions, in many situations this energy is not sufficient to entirely break the chemical bonds[6]. Therefore, to increase treatment efficiency, microwaves have often been combined with advanced oxidation processes (AOPs).

In this work, the efficacy of microwave-enhanced Fenton reaction for the treatment of methylene blue (MB) was tested under laboratory conditions. Operational parameters ($[H_2O_2]$, $[Fe^{2+}]$, $[H_2O_2]/[Fe^{2+}]$, and temperature (T)) were optimized to maximize removal of MB.

2. Materials and methods

2.1. Chemicals

MB was selected as a contaminant because it is non-biodegradable, extensively-used in textile industry[8], and widely-used to characterize the suitability of various materials for water and wastewater treatment[9]. MB ($C_{16}H_{18}N_3SCl \cdot 3H_2O$, > 97%) was acquired from Daejung Chemicals & Metals Co. (South Korea). Iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) (99%) was purchased from Yakuri Pure Chemicals Co. (Kyoto, Japan) and hydrogen peroxide (H_2O_2) (30%v/v) from Daejung.

2.2. Microwave reactor

We used a Microwave Accelerated Reaction System (MARS, CEM Corporation, 0–1,600 W power output, 2,450-MHz frequency, T range: 0–330°C) equipped with a T sensor. To contain the MB, we used 250-mL flat-bottom flask with a ground glass joint neck equipped with a magnetic stirrer (120 rpm). As a conventional heating reactor we used a flat-bottom flask in a shaking incubator (Model VS-8480SF, Vision Scientific Co., Korea). The total liquid volume was 200 mL. The initial [MB] was 200 mg/L (pH = 4.5). The pH was not adjusted. The resulting [MB] was measured immediately after treatment.

2.3. Analytical methods

MB decolorization was monitored using a UV-Vis Spectrophotometer (Biochrom., Libra S60, UK). The [MB] was measured at 645 nm. Total organic carbon (TOC) was determined using a TOC analyzer (TOC-VCPH, Shimadzu, Japan). Because reaction could continue after sampling, the whole procedure of sampling and measuring the absorbance and TOC was always finished in ≤ 15 min[10].

3. Results and discussion

3.1. Effect of H_2O_2 concentration

As $[H_2O_2]$ increased from 2.65 to 4.41 mM, the decolorization of MB increased from 22.7 to 99.1% (Fig. 1), because the quantity of OH· increases with $[H_2O_2]$ at 30°C, 1.5 min, and 0.18 mM Fe^{2+}. As $[H_2O_2]$ increased from 2.65 to 5.88 mM, the TOC removal of MB increased to 91.3%. However, at $[H_2O_2]$ ≥ 5.88 mM, the TOC removal efficiency decreased; this can be explained by the scavenging effect when using a high $[H_2O_2]$[7, 11, 12]. Addition of H_2O_2 influences the decomposition of organic compounds by the Fenton reaction. Generally, the degradation efficiency or rate of organic compounds increases as $[H_2O_2]$ increases until a critical $[H_2O_2]$ is achieved[12], but at $[H_2O_2]$ higher than the critical concentration, the degradation efficiency of organic compounds decreases as a result of the scavenging effect. The decolorization of MB is faster than mineralization[12].

MB decolorization at 30 min was almost constant at 3.38 ≤ H_2O_2 ≤ 3.68 mM. After the first 1.5 min, the decolorization of MB was 32.7% at 3.23 mM of H_2O_2, 34.8% at 3.38 mM, 60.9% at 3.53 mM, and 91.9% at 3.68 mM (Fig. 2). After 30 min of the reaction, it increased to 94.9% at 3.23 mM, 99.2% at 3.38 mM, 99.4% at 3.53 mM, and 99.6% at 3.68 mM..

H_2O_2 alone (without Fe^{2+}) or Fe^{2+} alone (without H_2O_2) could not degrade MB in this study[13, 14]. In the absence of these catalytic species, the Fenton's reaction does not generate extra OH·[6]. Of the two reagents, H_2O_2 is more critical because it directly affects the theoretical maximum mass of OH· generated[5].
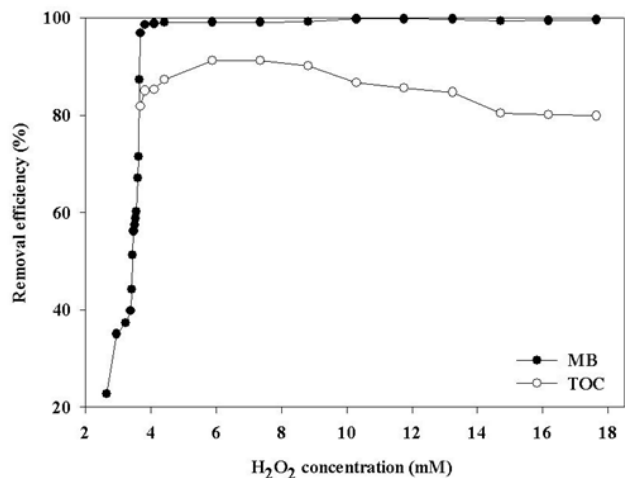
Fig. 1 Effect of H_2O_2 concentration on removal of methylene blue (MB) and total organic carbon (TOC) after 1.5 min at [Fe^{2+}] = 0.18 mM
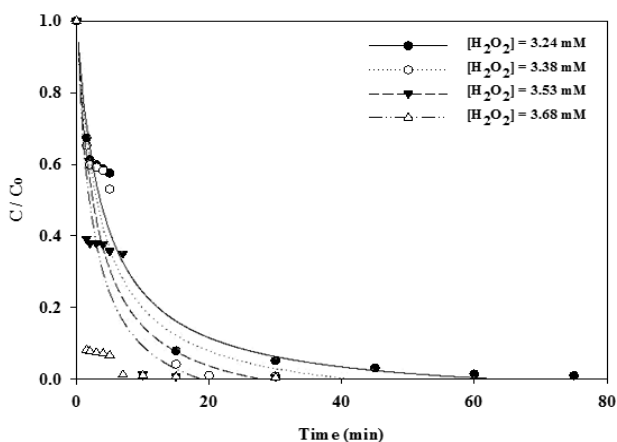

Fig. 3 Effect of Fe^{2+} concentration on removal of methylene blue (MB) and total organic carbon (TOC) after 1.5 min at [H_2O_2] = 4.41 mM

Fig. 2 Comparison between the experimental data and the kinetic model with H_2O_2 concentration at [Fe^{2+}] = 0.18mM

Fig. 4 Comparison between the experimental data and the kinetic model with Fe^{2+} concentration at [H_2O_2] = 4.41 mM

3.2. Effect of Fe^{2+} concentration

Decolorization of MB increased very rapidly with increasing [Fe^{2+}] from 0.07 to 0.18 mM at 30℃, 1.5 min, and 4.41 mM of H_2O_2 (Fig. 3). After the first 1.5 min, the decolorization was 24.0% at 0.07 mM of Fe^{2+}, 60.2% at 0.11 mM, 63.8% at 0.14 mM, and 98.5% at 0.18 mM (Fig. 4). After 5 min, decolorization increased to 40.8% at 0.07 mM, 62.6% at 0.11 mM, 67.9% at 0.14 mM, and 99.7% at 0.18 mM. Within the range studied, an increase in [Fe^{2+}] led to an increase in the MB degradation rate[14]. Increasing the [Fe^{2+}] accelerates the oxidation process, but also influences the microwave irradiation mechanisms[6]. However, the removal increase may be marginal when [Fe^{2+}] is high
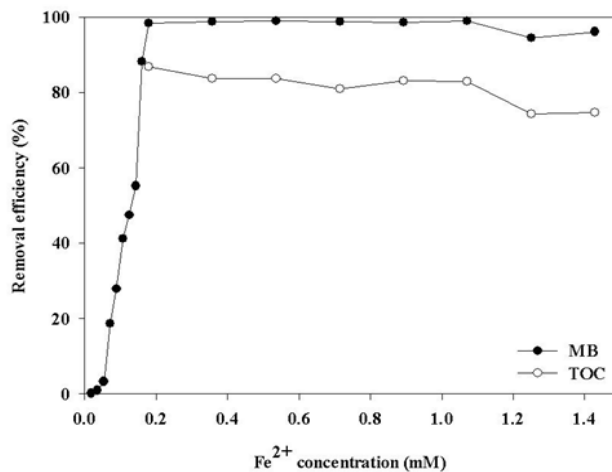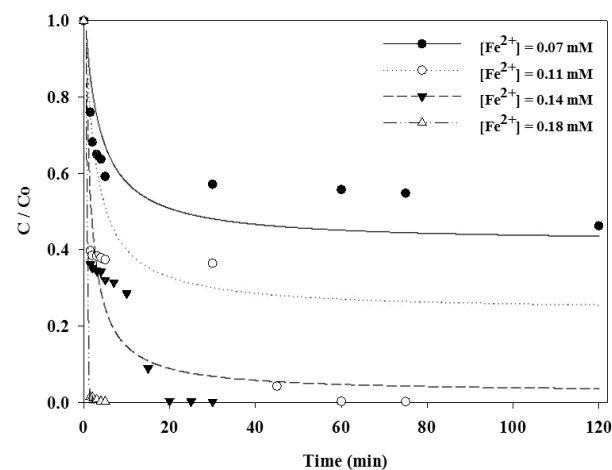
[5, 11]. Combining microwave irradiation with an oxidant is expected to stimulate free radical generation and to cause rapid polarization of the pollutant molecule[15].

3.3. Effect of [H_2O_2]/[Fe^{2+}]

To find the optimal [H_2O_2]/[Fe^{2+}] (mM/mM), MB removals were plotted against the [H_2O_2]/[Fe^{2+}] calculated for the experiments (Fig. 5). MB removal at 30℃ and 1.5 min remained almost constant (96.7–99.8%) for $3.5 \leq [H_2O_2] \leq 9.5$ mM and $0.35 \leq [Fe^{2+}] \leq 1$ mM. At doses lower than these ranges, MB removal

decreased; i.e. MB removal efficiencies were $\geq$ 95% at $[H_2O_2] \geq$ 3.5 mM and $3.5 \leq [H_2O_2]/[Fe^{2+}] \leq 17.3$, but $[H_2O_2]/[Fe^{2+}] \geq 20$ caused a decrease in MB removal. MB removals decreased when either $[H_2O_2]$ or $[Fe^{2+}]$ was superfluous, i.e. where the ratio was the lowest or the highest[16]. This results indicates that maximum MB removal requires both an appropriate $[H_2O_2]/[Fe^{2+}]$, and a sufficient amount of Fenton's reagent to produce adequate amount of OH[16]. To achieve maximum removal with minimum doses, the effect of $[H_2O_2]/[Fe^{2+}]$ ratio is important[16].

In previous studies the optimal $[H_2O_2]/[Fe^{2+}]$ ratio for removal of organics varied greatly depending on the types of organics and their loads. For composite wastewater from carpet dyeing, COD removal was greatest at $153 \leq [H_2O_2]/[Fe^{2+}] \leq 470$[16]. Color removal efficiency of Reactive Blue 19 was greatest at $[H_2O_2]/[Fe^{2+}]$ of 10 or 20 but not significant at higher ratios[17]. Maximal removal (45%) of textile wastewater (3,000 mg TOC/L) occurred at $[H_2O_2]/[Fe^{2+}] = 1.23$[18]. Maximal oxidation of triazophos occurred at $[H_2O_2]/[Fe^{2+}] = 44$[19]. Maximal removal of humic substances from landfill leachate occurred at $[H_2O_2]/[Fe^{2+}] = 6$[20].

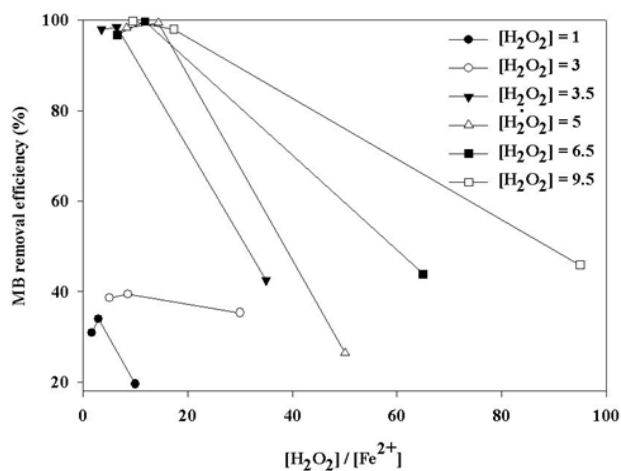**Fig. 5 Effect of $[H_2O_2]/[Fe^{2+}]$ on methylene blue removal after 1.5 min**

3.4. Effect of temperature

MB degradation rate increased with T[5, 20, 21] at $[H_2O_2] = 4.41$ mM and $[Fe^{2+}]=0.07$mM (Fig. 6). After 5 min at 90℃, 98% of initial MB was degraded. At low T the degradation slows considerably, particularly at 30℃[14]. Increase in T may increase the rate of OH generation and the probability of reaction between OH and MB molecules at low $[Fe^{2+}]$[20]. However, few studies have quantified the effect of T on the degradation rate[11, 22].
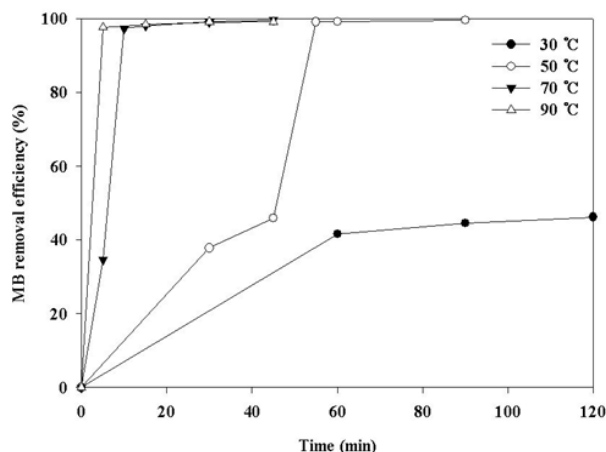

Fig. 6 Effect of temperature on methylene blue removal at $[H_2O_2] = 4.41$ mM and $[Fe^{2+}] = 0.07$ mM

3.5. Microwave and conventional heating oxidation process

During the microwave heating oxidation process, MB degradation of 99% was achieved within 1.5 min at 30℃, 4.41 mM H_2O_2, and 0.18 mM Fe^{2+} (Fig. 7). Using conventional heating at the same condition, 99% degradation of MB required 25 min. In the traditional Fenton process used in this study, MB conversion increased from 52.0% at 15 min to 97.4% at 25 min during the fast removal stage at 30℃, 4.41 mM H_2O_2, and 0.18 mM Fe^{2+} (Fig. 7). Thereafter, MB conversion increased slightly, to 99.6% at 60 min. When H_2O_2 in solution is exposed to microwave irradiation, it generates extra OH due to the excitation of molecules to high vibration and rotational energy levels [15], thereby enhancing MB degradation[6].
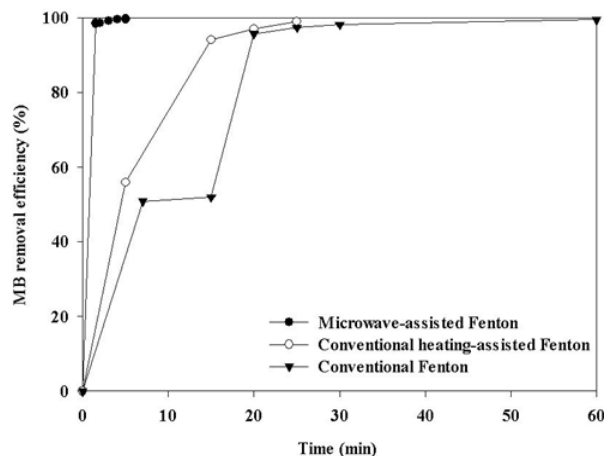

Fig. 7 Methylene blue removal efficiency with microwave-assisted, convention heating-assisted, and conventional Fenton reaction at $[H_2O_2] = 4.41$ mM and $[Fe^{2+}] = 0.18$ mM

3.6. Kinetics model for MB degradation by Fenton's process

The Fenton's oxidation mechanism involves several parallel and consecutive reactions[6]. For that reason, a complete kinetic study would involve solving a great number of differential equations. The Fenton's oxidation process is divided in two reaction steps, due to the mechanism complexity[6]. In a first step, the Fe^{2+} ions react very rapidly with H_2O_2 to form $OH^{\cdot}$ which reacts with the organic compounds, so they are decomposed quickly[14]. In the second step, the produced Fe^{3+} ions can also react with H_2O_2 to yield H_2O and thereby replenish the Fe^{2+}ions[14], so organic compounds are degraded more slowly than in the first step. These steps correspond to the observation that the MB degradation rate was very fast during the first minutes of reaction, then decreased (Fig. 7). Therefore, to stimulate the reaction kinetics of MB, we used a two-stage (rapid reaction stage followed by a retarded stagnant stage) mathematical model[23]:

$$\frac{C}{C_0} = 1 - \frac{t}{m + bt} \quad (1)$$

where C is the [MB] (mg/L) at time t (min), C_0 is the initial [MB] (mg/L), and m and b are characteristic constants. Taking the first derivative of Equation 1 and applying the limit when t à 0 reveals that $1/m$ correspond to the initial decay rate of MB:

$$\left(\frac{dC/C_0}{dt}\right)_{t \to 0} = \left(\frac{-m}{(m+bt)^2}\right)_{t \to 0} = -\frac{1}{m} = -r_0 \quad (2)$$

Taking the limit of Equation 1 as $t \to \infty$ reveals that $1/b$ is related to the maximum oxidation degree attained:

$$\frac{1}{b} = 1 - \left(\frac{C}{C_0}\right)_{t \to \infty} \quad (3)$$

Fenton's oxidation results seem to be adequately predicted by this model ($0.97 \leq R^2 \leq 1.00$) (Table 1). The initial reaction rate ($1/m$) was higher under microwave irradiation than under conventional heating, but the maximum oxidation degree ($1/b$) was similar in the two cases[6].

During microwave-assisted oxidation, the initial degradation rate increased as initial $[Fe^{2+}]$ increased. The variation of $1/m$ with $[H_2O_2]$ was not uniform, resulting in very similar values for

concentration between 3.24 and 3.53 mM. The term $1/b$ seems to be almost independent of the studied parameters, because for sufficiently long reaction times its value indicated that no MB remained in solution after MB-assisted Fenton's oxidation[6].

Apparent order dependencies can be estimated, assuming the following power-law equations[6, 14, 24]:

$$m = A[H_2O_2]^a[Fe^{2+}]^b = 727.78[H_2O_2]^{-12.7}[Fe^{2+}]^{-7.03} \quad (4)$$

$$b = B[H_2O_2]^c[Fe^{2+}]^d = 0.75[H_2O_2]^{-0.43}[Fe^{2+}]^{-1.01} \quad (5)$$

where A and B are constants, and a, b, c, and d are the apparent reaction orders. Equations 4 and 5 allow prediction of the decay curves at any conditions within the studied range. $[H_2O_2]$ seems to have the greatest weight in the degradation rate (Equation 4), but the weights of each parameter in the maximum oxidation degree equation (Equation 5) are small when compared to the initial reaction rate. The Chan and Chu model fit the data well (Fig. 2 and 4)[6].

Table 1 Kinetic parameters of the proposed model for the degradation of methylene blue

$[H_2O_2]$ (mM)	$[Fe^{2+}]$ (mM)	H_2O_2/Fe^{2+}	$1/m$ (min^{-1})	$1/b$	R^2
4.41	0.07	61.76	0.16	0.51	0.987
4.41	0.11	41.18	0.29	1.01	0966
4.41	0.14	30.86	0.43	1.08	0.986
4.41	0.18	24.69	30.68	1.00	1.000
3.24	0.18	18.14	0.23	1.06	0.997
3.38	0.18	18.93	0.22	1.20	0.974
3.53	0.18	19.76	0.47	1.08	0.982
3.68	0.18	20.60	4.64	1.00	0.999

4. Conclusions

Microwave-assisted Fenton's oxidation led to faster and more complete degradation of MB than did the traditional Fenton's reaction. The TOC removal efficiencies of MB were greatly influenced by $[H_2O_2]$, $[Fe^{2+}]$, $[H_2O_2]/[Fe^{2+}]$, and T. The best results (96.7–99.8% degradation) were obtained at $3.5 \leq [H_2O_2] \leq 9.5$ mM, $0.35 \leq [Fe^{2+}] \leq 1$ mM, $3.5 \leq [H_2O_2]/[Fe^{2+}] \leq 17.3$, 30°C, and 1.5 min. A kinetic

model was developed and applied to the results, and fit the experimental data well. Microwave-assisted Fenton's oxidation is a promising method to reduce the time required to degrade recalcitrant organics.

Acknowledgements

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