



Structural characterization of natural organic matter and its impact on methomyl removal efficiency in Fenton process



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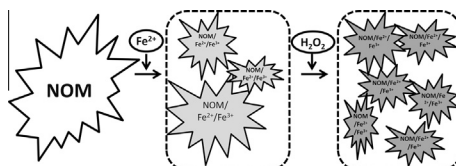
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HIGHLIGHTS

- The most methomyl removal by Fenton process was found at $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ of 2 mM:2 mM.
- NOM presence could enhance the methomyl removal by Fenton process.
- The reaction of Fe^{2+} with humic acid broke the humic acid into smaller fractions.
- More $\cdot\text{OH}$ was generated than consumed by the presence of humic acids.
- Enhanced methomyl removal was observed in the presence of humic acids.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aimed to characterize the NOM structural variation during Fenton process, in which the methomyl and humic acid were selected as the investigated compounds. The preliminary degradation experiments were conducted at various H_2O_2 and Fe^{2+} concentrations without the presence of NOM to determine the applied Fenton reagent dosages for subsequent NOM impact on Fenton degradation. The methomyl removal at 80% was observed at the Fenton reagent ratio ($[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$) of 1 while Fe^{2+} concentration was no less than 2 mM. In the presence of NOM, the methomyl removal by Fenton process was further enhanced apparently. The NOM used in this study was found to be a macromolecule with tryptophan-like and tyrosine-like functional groups through fluorescence spectrometry analysis. The addition of ferrous ions in the NOM solution initiated the reactions between $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples and NOM molecules, breaking the NOM into smaller organic fractions. These organic fractions were further oxidized into even smaller molecules by hydroxyl radicals after H_2O_2 addition. The NOM might compete with methomyl for hydroxyl radicals, and enhance the catalytical generation of hydroxyl radicals by reducing Fe^{3+} to Fe^{2+} at the same time. Apparently, the increase in $\cdot\text{OH}$ generation was more than the $\cdot\text{OH}$ consumption by NOM presence, resulting in the observed enhancement of methomyl removal.

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1. Introduction

Natural organic matter (NOM) is a heterogeneous combination of aromatic and aliphatic structures containing various functional

groups such as carboxyl, phenol, enol, alcohol, carbonyl, amine or thiol. NOM is ubiquitous and affects physical, chemical and biological processes in the environment (Fukushima et al., 2001; Nie et al., 2010; Chai et al., 2012). In natural water bodies, NOM may act as the scavenger to compete with other organic chemicals for reactive oxidants. This competing phenomenon impacts significantly on the aqueous organic contaminant removal when physi-

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cochemical processes were employed to improve the aquatic environment (Katsumata et al., 2008; Romero et al., 2011; Wu et al., 2011).

For water and wastewater treatment, the physicochemical process was often chosen because of their consistency in treatment efficiency and ease in system maintenance as compared to biological processes (Athanasopoulos and Athanasopoulos, 1998; Oller et al., 2011). As the aquatic contaminants were found more and more persistent and difficult to remove through conventional biological processes, the adoption of advanced oxidation processes (AOPs) in wastewater treatment processes became a popular alternative (Badawy et al., 2009; Deblonde et al., 2011; Dirany et al., 2012). Among the frequently-applied AOPs, Fenton process is considered of the most advantages due to its relatively low cost, ready availability of H_2O_2 , and the abundant existence of iron in the environment. Fenton reaction consists of the participation of H_2O_2 in a series of redox reactions catalyzed by Fe^{2+} , which provoke the generation of hydroxyl radicals to oxidize the target contaminants without selectivity.

In the literature, many studies regarding the removal of natural organic matter and other co-dissolved organic contaminants by Fenton reaction were reported. In the study by Lindsey and Tarr (2000), the degradation of aqueous aromatic compounds by Fenton reaction was inhibited by the presence of dissolved fulvic acids due to the possible formation of un-reactive complexes through molecular bindings between aromatic compounds and fulvic acids. Southworth and Voelker (2003) found that the reactions between Fe and fulvic acids inhibited the formation of hydroxyl radicals in photo-Fenton process. In the application of Fenton-like process to phenol-contaminated soil remediation, Romero et al. (2011) reported that the NOM might compete with phenols for the hydroxyl radicals, reducing phenol removal efficiency by decreasing the NOM sorption ability through external surface modification. Owing to the variation in molecular structure, the NOM molecules might be degraded to different oxidation levels by reacting with the hydroxyl radicals in the photo-Fenton process (Fukushima et al., 2001; Katsumata et al., 2008). In the study by Fan et al. (2011), the NOM was found capable of enhancing the Fenton degradation efficiency in neutral environment. Apparently, the presence of NOM exhibits significant impacts on contaminant removal efficiency by Fenton-related processes.

To explore the role of NOM in Fenton degradation system, this study aimed to investigate the impact of NOM presence on the organic contaminant removal by Fenton process in the acidic environment. The pesticide of methomyl was selected as the target contaminant because it has been used extensively in agricultural activities due to its chemical characteristics of significant toxicity, bioaccumulation and persistence. Its residual in the environment might become the long term contamination sources and pose a serious threat to the aquatic environment. The humic acid (HA) was chosen as the representative NOM. A preliminary study of the methomyl degradation at different Fenton reagent dosages in acidic environment was conducted to determine the Fenton reagent concentrations used for subsequent NOM-influenced Fenton degradation experiments. The competitive effect between methomyl and humic acids was evaluated. The humic acid structure was characterized using fluorescence spectrometer, scan electron microscopy (SEM), size exclusion chromatography (SEC), and Fourier transform infrared (FTIR) spectroscopy.

2. Materials and methods

2.1. Reagents and chemicals

The reagent grade methomyl with 96.7% purity was purchased from CHEM SERVICE. The humic acid was purchased from AL-

DRICH. The FeSO_4 and H_2O_2 used were reagent grade chemicals purchased from SANTOKU and SHOWA, respectively. The water used in the experiments was nanopure water. For pH adjustment, NaOH and H_2SO_4 used were reagent grade chemicals purchased from Riedel-de Haen and JB Baker, respectively. The quenching agent of KI was purchased from SIGMA.

2.2. Experimental procedures

The preliminary Fenton degradation experiments were conducted in the 250 ml beakers under ambient temperature of $22 \pm 2^\circ\text{C}$ at pH 3. The initial methomyl concentration was 20 mg L^{-1} , which was comparable to the observed aqueous concentration in the agricultural areas in Taiwan. For the degradation experiments, initial concentrations of Fe^{2+} were 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM, and initial H_2O_2 concentrations were 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 mM. At a given Fe^{2+} concentration, the degradation experiments were conducted at each of these H_2O_2 concentrations. For the Fe^{2+} concentration of 2.5 mM, an additional experiment was performed at the H_2O_2 concentration of 2.5 mM. With the consideration of experimental design concept, the applied Fenton reagent dosages were determined based on the previous study by Fan and Liao (2009), following the suggestion by Duesterberg and Waite (2007) and Kwan and Voelker (2002), to control the hydroxyl radical concentration at a comparatively low level to avoid considerable target removal in the beginning of degradation experiments. The Fenton degradation was initiated by adding H_2O_2 into the aqueous solution containing methomyl and Fe^{2+} . The methomyl concentration was monitored by taking an aliquot of the tested solution at 0, 2, 5, 10, 15, 20, 25 and 30 min after the reaction took place. The quenching agent of 0.1 M KI was added to stop the reaction immediately after the sample was collected.

For methomyl degradation in the presence of humic acid, the humic acid concentrations were 2.5, 5, and 10 mg L^{-1} , and the Fenton reagent ratios (i.e., H_2O_2 to Fe^{2+}) were controlled at 4 mM:2 mM and 2 mM:2 mM. This humic acid concentration was determined based on the study by Hummel (1997), who reported the humic acid concentration in natural water bodies between 0.5 and 30 mg L^{-1} . The Fenton reagent ratios were determined according to the results of the preliminary Fenton degradation experiments.

2.3. Sample analysis and characterization

The samples were analyzed using Waters Alliance HPLC and UV detector. The column used was Waters PAH C18 column. The sample volume injected was $20\text{ }\mu\text{L}$, and the flow rate was 1 ml min^{-1} . The mobile phase was 45% H_2O and 55% methanol. The UV detector wavelength was 238 nm. The characteristics of the humic acid were inspected by the excitation/emission matrix (EEM) obtained using fluorescent spectrometer (Perkin Elmer LS55) scanning from 200 to 600 nm wavelength for both excitation and emission at the slits of 5 nm. The scan speed was 120 nm min^{-1} and the wavelength increment was 10 nm. The average molecular weight of the humic acid was analyzed with size exclusion chromatography by injecting aqueous samples collected before and 30 min after the degradation reaction taking place. The high pressure liquid chromatography with P1000 pump and UV1000 detector was purchased from Thermo Scientific. The detector wavelength was 254 nm and the mobile phase was 0.1 M NaOH aqueous solution at the flowrate of 1 ml min^{-1} . The columns (PSS-MCX 1 pre-column with $8 \times 50\text{ mm}$, and 2 SEC columns (1000 and 1000000 A), $8 \times 300\text{ mm}$ each) were purchased from Polymer Standards Service GmbH, Germany. The poly (styrene sulfonate) sodium salts with molecular weights of 1100, 3610, 63900 and

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