RAPID DEGRADATION OF METHYL ORANGE
WITH NANOSCALE ZEROVALENT IRON PARTICLES

Yang-Hsin Shih1*, Chih-Ping Tso2 and Li-Yuan Tung2

1 Department of Agricultural Chemistry
National Taiwan University
Taichung 106, Taiwan

2 Department of Soil and Environmental Sciences
National Chung Hsing University
Taichung, Taiwan

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ABSTRACT

Refractory azo-dye compounds used in the textile industry are commonly detected in textile wastewater. In this study we investigated the reduction kinetics and efficiency of methyl orange, one of azo-dyes, with laboratory synthesized nanoscale zero-valent iron, ZVI (NZVI) particles in relation to the NZVI dosage, temperature and pH. The degradation of methyl orange with NZVI occurs at a much faster rate than with microscale ZVI. Increasing the dose of NZVI particles enhanced the decolorization rates of methyl orange. The reaction rate constants decreased with increasing solution pH but increased with increasing temperature. The activation energy was estimated to be 22.7 kJ mol⁻¹. These findings demonstrated the fast removal of azo-dye compound with NZVI and the advantage of the synthesized NZVI particles to treat azo-dye-contaminated wastewater.

INTRODUCTION

Dye industry wastewater from the textile industry has been considered as an important source of water pollutants in the world because dyes are highly colored and are refractory to degradation. Azo dyes constitute about a half of global production (700,000 t y⁻¹) and during dyeing operation processes, about 15% of them end up in wastewaters [1]. Aromatic azo-dyes, with the azo group (-N=N-), comprise about half of the total world dye market [2,3]. Azo-dyes are also a major class of synthetic organic compounds released by many industries such as paper, plastic, leather, food, cosmetic and pharmaceutical industries [3,4]. These effluents result in significant environmental pollution. Furthermore, azo-dye compounds were recognized as potential carcinogens [5,6]. Abatement of dyes is a required part of wastewater treatment.

Azo-dye effluents are highly resistant to microorganisms so that their reduction by using conventional biological treatments is generally ineffective. The dye wastewaters are also resistant to destruction by physical-chemical treatments such as activated carbon sorption, UV light-degradation and chemical oxidation-reduction treatments, especially in a high effluent concentration [7]. Recently, zero-valent iron (ZVI) has been intensively investigated for remediation of a wide range of contaminants such as chlorinated organic compounds [8-10], toxic metals [11-13], and inorganic compounds [14,15]. In order to remove complex dye compounds from the wastewater, the degradation of azo-dyes by microscale ZVI (MZVI) powder has also been examined over the last decade [7,16-17].

Nanotechnology has been extended to the waste treatments in the recent years. Nanoscale ZVI (NZVI) particles have emerged promptly in the treatments of several toxic chemicals in the environment [18]. Due to the high surface area of NZVI than that of the MZVI, the nanoscale iron particle exhibits an enhanced reactivity [19] for the degradation of halogenated organic contaminants, such as halogenated hydrocarbons [2] and polychlorinated biphenyls [2,20]. Rapid decolorization of the azo-dyes by use of NZVI particles could effectively achieve the removal and may not need further treatments.

In this study we investigated the degradation of an azo-dye compound, methyl orange, by using both laboratory-synthesized NZVI and commercial MZVI particles and compared their degradation kinetics and
efficiencies. We also evaluated the dosage of NZVI, the reaction temperature and the solution pH on the degradation of methyl orange with NZVI.

**EXPERIMENTAL METHODS AND MATERIALS**

1. **Preparation of Nanoparticles**

NZVI was chemically synthesized in the laboratory by reduction of 1 M ferric chloride (Backer) solution with 1.6 M sodium borohydride (Riedel-de Haën) solution at ambient temperature with vigorous stirring [2,21-22]. Pure water was double-distilled and deionized with a Milli-Q water purification system (Millipore). The ferric iron was reduced to NZVI particles. NZVI particles were washed with acid and deionized water three times to remove the residual reagents. During the period of the reaction process, ferric iron was reduced, with the ZVI particles precipitated instantly, according to the following reaction [2]:

$$\text{Fe(H}_2\text{O)}_6^{3+} + 3\text{BH}_4^- + 3\text{H}_2\text{O} \rightarrow \text{Fe}^0 \downarrow + 3\text{B(OH)}_3^- + 10.5\text{H}_2$$  

(1)

The particle size and morphology of the resulting NZVI particles were determined using a field emission scanning electron microscope (FE-SEM, JEOL JEM-2010). Analysis of nanoscale Fe particles with an energy dispersive spectrometer (EDS) was used to determine the surface characteristics. X-ray diffraction (XRD) spectroscopy of NZVI was carried out under an anaerobic condition using the Synchrotron XRD in the National Synchrotron Radiation Research Center, Taiwan. Surface area was determined from the nitrogen adsorption data by an ASAP2100 analyzer (Micrometrics Instrument Corporation, USA).

2. **Batch Experiments and Analytic Methods**

Batch experiments were conducted to investigate the reaction kinetics of the NZVI and MZVI particles (about 50 μm in size and 90% in purity, Kanto Chemical) for the degradation of methyl orange (C14H14N3NaO3S, 99% purity, Arcos). The structure and adsorption spectrum of methyl orange are shown in Fig. 1. The experiments were carried out in 20 mL amber vials sealed with Teflon lined septa after adding 10 mL of the methyl orange solution at about 25 mg L⁻¹ and a suitable amount of NZVI or MZVI particles as indicated in the following experiments. The initial pH value in the solution of methyl orange was adjusted by HCl and NaOH (Backer) for the experiments at fixed pHs. The reaction vials for the degradation of methyl orange with MZVI was carried out on a rotary shaker (150 rpm). No mixing actions were performed for the vials with NZVI particles. The concentrations of methyl orange were quantified by UV/Vis spectrophotometer (UNICO 2808) under 464 nm. The concentrations of the dissolved iron were determined by an atomic absorption spectroscopy.

The degradation rates can be described as a pseudo-first order reaction.

**RESULTS AND DISCUSSION**

1. **Characteristics of Synthesized NZVI Particles**

The particle size of the NZVI particles was in the range of 50-100 nm (Fig. 2). The FE-SEM image also reveals that iron nanoparticles tend to form a chain-like aggregate due to the magnetic attractive force be-
between particles. These chain-like nano iron aggregates were also observed by others [2,22,23]. The specific surface area of the synthesized nanoiron, as determined by the BET method, was ca 29 m² g⁻¹. The zerovalent type of nanoiron particles was confirmed by EDS and XRD (Fig. 3). Some iron oxides were observed in the EDS image due to the sample preparation process. The NZVI without iron oxides was identified by the XRD spectrometer under anoxic conditions.

2. Degradation Kinetics and Efficiencies of Microscale and Nanoscale Zerovalent Iron Particles

The degradation of methyl orange with NZVI occurred more efficiently than that with MZVI, as shown in Fig. 4. During the experiments, the NZVI particles were well suspended in the reaction vial in the beginning, whereas MZVI particles were largely settled to the bottom of the vial. After 10 min, the color in the vial with NZVI was clearly decreased but not observed for MZVI. Methyl orange was completely decolorized by NZVI after 24 min, whereas the orange color did not appear to change with MZVI even though the amount of MZVI used in the experiments is 8.3-fold larger than that of NZVI.

For the removal efficiency, more than 90% of methyl orange was degraded by about 3 g L⁻¹ of NZVI particles in 24 min and only about 25% degraded by about 25 g L⁻¹ of the MZVI particles (Fig. 4). Also, greater degradation kinetics and higher removal efficiency were observed for NZVI without mixing on a shaker as compared to those for MZVI with mixing at 150 rpm. The first-order rate constant (k) for NZVI was 0.34 min⁻¹ for methyl orange. In comparison, the value of k for commercial MZVI was only 0.05 min⁻¹. The reactivity of methyl orange with the NZVI is about 6.8-fold higher than that with the MZVI. Comparing the results from our study and similar studies reported in the literature, NZVI particles were clearly more efficient than microscale particles for degrading several contaminants, such as trichloroethene [2] and nitrate [24]. A much greater specific surface area for NZVI (e.g. 26 m² g⁻¹ in this work) as compared with the specific surface area for MZVI (0.2 m² g⁻¹) gives an explanation to the high reduction rate of the NZVI with this azo-dye compound, methyl orange.

3. Effect of NZVI Dosage

The effect of the NZVI dosages on the degradation rate of methyl orange is shown in Fig. 5. It was found that when the NZVI dosage increased, the concentration of methyl orange decreased rapidly and the degradation efficiencies increased from about 20 to 100% over the first 10 min. The increased NZVI amount in the degradation reactions enhanced the degradation efficiency. The degradation rate constants are 0.067, 0.29, 0.34 and 0.83 min⁻¹ for 1, 2, 3 and 5 g L⁻¹ NZVI dosage, respectively. A good relationship was
also found between the degradation rate and the amount of NZVI applied (1 to 5 g L\(^{-1}\)) in this study. According to the theoretical calculation for the degradation of about 10 mg L\(^{-1}\) methyl orange, only about 2 mg L\(^{-1}\) of dissolved iron could be produced. This concentration of dissolved iron did not exceed the effluent standard in Taiwan (10 mg L\(^{-1}\)). However, the measured residual concentrations of dissolved iron increased with increasing of the NZVI dose (2-5 g L\(^{-1}\)) (Fig. 6). It could be resulting from the further oxidation of iron by the exposure of oxygen during the experiments. In case the residual iron concentration was over the standard, further treatments such as coagulation and precipitation processes could be needed.

Increasing the dose of NZVI particles enhanced the decolorization rates of methyl orange. This is expected because, with more NZVI particles used, there will be more surface sites for reaction with methyl orange to accelerate the degradation of methyl orange. Hou et al. [17] also found that the degradation kinetic constants of three azo dyes increased with increasing dosage of the NZVI.

4. Effect of pH

The aqueous pH could affect the dye degradation reactions for ZVI due to the hindrance of ferrous hydroxide produced from ferrous ions and hydroxyl ions in the oxidation of ZVI surface in a high pH solution. The initial pH effect on methyl orange degradation is illustrated in Fig. 7. The observed degradation results at initial pH 3.1, 6.8 and 9.2 indicated that the degradation kinetics and the final removal efficiency of methyl orange increased with a decrease in pH. The calculated pseudo-first-order degradation rate constants are 1.1, 0.45 and 0.43 min\(^{-1}\) for pH 3.1, 6.8 and 9.2, respectively. The increase in concentration of hydrogen ions would enhance the reduction degradation reactions of azo compounds because hydrogen ions are involved in the reductive reaction by ZVI. Furthermore, the lower aqueous pH may help to reactivate the oxidized iron layer, and then enhance the degradation reaction on the surface of NZVI particles [24].

On the other hand, the methyl orange molecule exists as an anion in water at around and above pH 7, because of the dissociation of the sodium ion. Under an acid condition, amphoteric methyl orange molecules are formed because hydrogen ion would be attached to the nitrogen atom of azo group [25]. Since the zero point of charge of NZVI is around 8.1 [26], the electrostatic repulsion between the anionic methyl orange molecules and negative NZVI in an alkaline condition could not enhance their collisions to increase the degradation process. However, at an acid condition, the hydrogen ion at an azo group could enhance the degradation of methyl orange with NZVI.

Yang and Lee [27] also showed that the degradation of nitrate by NZVI was an acidity-driven process.
The degradation rate constants of azo dyes with commercial MZVI also increased with a decrease in the pH values [28]. The enhanced reduction of azo dyes with an increase in H^+ concentration was also found by Suzuki et al. [29].

5. Effect of Temperature

The effect of temperature on the reaction kinetics of methyl orange with NZVI was investigated over the temperature range of 7 to 45 °C, as shown in Fig. 8. The degradation efficiencies were about 48, 83 and 96% for 7, 25 and 45 °C after 20 min of reaction time, respectively. It is indicated that azo-dye degradation efficiency increased with increasing temperature in the reaction. The rate constants of methyl orange with NZVI system at 7, 25 and 45 °C were estimated to be 0.19, 0.48 and 1.52 min⁻¹, respectively. Lien et al. [26] also indicated that temperature is clearly an important parameter to promote the removal of perchlorate with NZVI from aqueous solution.

The Arrhenius equation may be used to describe the relationship between rate constants and temperature:

\[ k = Ae^{(-E_a/RT)} \]  

where \( k \) is the rate constant, \( A \) is a frequency factor, \( E_a \) is the activation energy, \( R \) is ideal gas constant, and \( T \) is the absolute temperature.

A plot of \( \ln k \) vs. \( 1/T \) using a linear least-square analysis is shown in Fig. 9. The estimated activation energy for the degradation of methyl orange by NZVI is approximately 23 kJ mol⁻¹. This small activation energy implies that the degradation of methyl orange by NZVI particles requires a relatively low energy, which is similar to the observed reduction degradation of chlorinated compounds by others [24,30]. It also implies that the small temperature effect on the decolorization reactions of NZVI for methyl orange in treatment process.

CONCLUSIONS

The degradation of methyl orange, one of azo-dye compounds, with the NZVI in aqueous solution was investigated. As compared to the degradation with MZVI particles, faster degradation kinetics and higher removal efficiencies were observed for NZVI particles. The degradation kinetic constants of methyl orange increased with an increase in NZVI dosage and the reaction temperature, but decreased with an increase in solution pH. Only a small activated energy (23 kJ mol⁻¹) is needed for the removal of methyl orange with NZVI particles, suggesting a small temperature effect for the decomposition reaction. These results have clearly elucidated that methyl oranges can be rapidly decolorized by NZVI particles and thus the use of NZVI could facilitate the removal of azo-dyes in wastewater.

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