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Kinetics of Solvent Blue and Reactive Yellow removal using microwave radiation in combination with nanoscale zero-valent iron

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ABSTRACT

We investigated the efficiency and kinetics of the degradation of soluble dyes over the pH range 5.0–9.0 using a method employing microwave radiation in combination with nanoscale zero-valent iron (MW–nZVI). The nZVI particles (40–70 nm in diameter) were prepared by a liquid-phase chemical reduction method employing starch as a dispersant. Compared to the removal of Solvent Blue 36 and Reactive Yellow K-RN using only nZVI, more rapid and efficient dye removal and total organic carbon removal were achieved using MW–nZVI. The dye removal efficiency increased significantly with decreasing pH, but was negligibly affected by variation in the microwave power. The kinetics of dye removal by MW–nZVI followed both an empirical equation and the pseudo first-order model, while the kinetics of dye removal using nZVI could only be described by an empirical equation. It was also concluded that microwave heating of the dye solutions as well as acceleration of corrosion of nZVI and consumption of Fe(II) were possible reasons behind the enhanced dye degradation.

Introduction

Textile dyeing and processing is one of the pillar industries of China, especially the Shandong Province, which is located on the eastern line of the South-to-North Water Transfer Project of China. Therefore, strict water pollutant discharge standard DB37/599-2006 (Shandong Environmental Protection Agency, 2006) must be adhered to by the textile factories located in this region to avoid enforced discontinuation of production by the government agencies. Moreover, the textile dyes commonly used in the textile industry exhibit anti-oxidation and anti-photodecomposition properties, and give high-strength chemical oxygen demand (COD) and high chroma wastewater (Tichonovas et al., 2013), making the decolorization of dyeing wastewater much more difficult, thus leading to considerable environmental impact on surface water (Comparelli et al., 2005; Gupta et al., 2012; Krissanasaeranee et al., 2010). Hence, a rapid and efficient technique for dye removal is not only desirable but also imperative for the survival of textile factories located along the eastern line and the water security of the Water Transfer Project.

Over the past few decades, degradation of dyes by zero-valent iron (ZVI) particles, especially nanoscale ZVI (nZVI), has emerged as one of the latest innovative technologies for dye wastewater treatment and environmental remediation (Bigg and Judd, 2001; Bokare et al., 2008; Cao et al., 1999; Chang et al., 2006; Epolito et al., 2008; Fan et al., 2009; Feng et al., 2000; Lin et al., 2008; Liu et al., 2007; Mu et al., 2004; Nam and Tratnyek, 2000; Perey et al., 2002; Shu et al., 2007, 2010; Zhang et al., 2005). In addition to the application of ZVI or nZVI to dye wastewater treatment, combinations of ZVI with various methods have also been attempted. Recently, microwave (MW) assisted methods such as MW-UV (Horikoshi et al., 2002, 2004b), MW-Fenton (Gromboni et al., 2007), MW-H_2O_2 (Klán and Vavrik, 2006; Prasannakumar et al., 2009), and

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MW-$K_2S_2O_8$ (Lee et al., 2009) have gained popularity, as indicated by numerous publications (Remya and Lin, 2011a). These studies concluded that MW radiation could enhance the efficiency of advanced oxidation processes for the degradation of organic pollutants (Gromboni et al., 2007; Yang et al., 2009; Zhang et al., 2007; Zhanqi et al., 2007).

The removal of organics using MW radiation in combination with ZVI and nZVI (henceforth denoted as MW–ZVI or MW–nZVI) has also gained interest in the last few years, because it provides fast and effective degradation of organic wastewater without abiotic reduction and oxidant dosage. Oh et al. (2006) reported first that 98% of perchlorate in water was removed by cast iron in 1 hr *via* microwave heating at pH 7.4. Jou (2008) degraded 1000 mg/L of pentachlorophenol using 700 W MW power and 0.5 g/L ZVI, achieving a removal efficiency exceeding 99% in 30 sec. Lee et al. (2010) reported that MW–nZVI could reduce the chlorobenzene activation energy by 6.1 kJ/mol and increase chlorobenzene removal efficiency 4.1 times. Furthermore, Lee and Jou (2012) found that nZVI with the application of MW radiation had greater ability to reduce the chlorobenzene activation energy than commercial micron-sized iron particles. Fu et al. (2010) developed a novel method of zero-valent iron/activated carbon combined with microwave discharge electrodeless lamp/sodium hypochlorite to remove Reactive Red 195, and obtained 100% color removal efficiency and 82% COD removal efficiency. Remya and Lin (2011b) found that complete carbofuran degradation could be accomplished in 5 min by MW–ZVI at pH 10 and 80°C.

The removal of dye from wastewater is a major concern, especially in the sensitive area along the South-to-North Water Transfer project of China. Although it has been accepted that MW–nZVI is a highly efficient method for the removal of organics, to the best of our knowledge, the removal of Solvent Blue 36 and Reactive Yellow K-RN from aqueous solution by MW–nZVI has not been reported previously. Hence, to advance our understanding of the reduction of dyes in the environment, we designed various aqueous systems to investigate the kinetics of the removal of these two dyes *via* MW–nZVI. The effects of key parameters including nZVI dosage, initial pH, and temperature on the dyes removal were examined to study the removal kinetics.

1. Materials and methods

1.1. Materials

Analytical grade reagents were used in all cases (except when noted) and were purchased from Shanghai Chemical Reagents Company, Shanghai, China. Organic dyes, namely, Solvent Blue 36 ($C_{20}H_{22}N_2O_2$, purity: ≥98%) and Reactive Yellow K-RN ($C_{21}H_{17}ClN_8O_7S_2$, purity: ≥98%), which were obtained from Liaocheng Sanhe Textile Co., Ltd., Shandong, China, were used without any purification as the target contaminants. The molecular structures of these organic dyes are shown in Fig. 1. All solutions were prepared using 18 MΩ cm ultrapure Milli-Q water (MQ) and stored in the dark at 4°C when not in use. All glassware and plastic ware were soaked in 5% (V/V) HCl for several days and rinsed thoroughly with MQ before use. All experiments were performed under conditions in which exposure to light was minimized by wrapping the reaction vessel with a dark cloth.

A background solution containing 2.0 mmol/L $NaHCO_3$ and 0.1 mol/L NaCl was prepared one week prior to the commencement of each experiment to ensure that equilibrium between the background solution and the atmosphere was reached. 0.1 mol/L Fe(III) solution, 0.16 mol/L $NaBH_4$ solution, 50 mg/L Solvent Blue 36 (hereafter, Blue) stock solution and 60 mg/L Reactive Yellow K-RN (hereafter, Yellow) stock solution were prepared prior to use. Starch was vacuum-dried for 6 hr at 50°C before use.

1.2. Preparation of nanoscale zero-valent iron

The nZVI particles were prepared based on a liquid-phase chemical reduction method (Joo et al., 2004; Wang and Zhang, 1997). However, starch was added to the 0.1 mol/L Fe(III) solution as the dispersant, using an starch-to-iron mass ratio of 0.65:1. To fabricate sufficient nZVI particles for the dye-removal experiments, 500 mL of a mixed solution of Fe(III) and starch was placed into a 1 L conical flask for each experiment, and N_2 was then pumped into the solution for 3 hr to eliminate O_2. In the next step, the 0.16 mol/L $NaBH_4$ solution was dropped into the reaction vessel at a rate of 2 drops/sec using a dropping funnel. Ferric iron was then reduced and black nZVI particles were precipitated at ambient temperature under stirring, according to the following reaction:

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0(s) + 3B(OH)_3 + 10.5H_2. \quad (1)$$

$NaBH_4$ was continually added until no further formation of nZVI was observed. The freshly prepared nZVI was quickly collected on a 0.45-μm membrane filter by filtration under suction and was sequentially washed three times using 10^{-4} mol/L HCl, MQ, and anhydrous ethanol for the removal of iron oxides, soluble ions, and water molecules, respectively. The wet nZVI was immediately vacuum-dried at 60°C for 6 hr. The weight of the nZVI particles produced in this way was more than 2.5 g with a consistent yield of ≥89%.

1.3. Kinetics of dye removal by MW–nZVI

The removal of dyes from the background solution using MW–nZVI was performed in a 2.45-GHZ MCR-3 microwave chemical reactor (Yuhua Instrument, Gongyi, Henan, China) equipped with a condenser tube and a stirring apparatus. Various amounts of nZVI were added to the 250 mL 50 mg/L Blue solution or 60 mg/L Yellow solution with varying pH (5.0, 7.0, and 9.0) in Pyrex® vessels (500 mL conical flask). The pH value was measured using a PHS-3C pH meter (Leici Instrument, Shanghai, China) combined with a glass electrode and Ag/AgCl reference. It should be noted that the pH was adjusted to the desired value without adding any buffer, because the presence of a buffer was anticipated to affect the decolorization reactions between the dyes and nZVI, though this was not proved in this study. After completion of the reactions, the pH of the dye solutions was evaluated again to confirm that there was a little change (±0.5) in the pH. In this study, the initial pH values were taken as the "true" values of the investigated solutions. After the addition of nZVI, dye solutions were immediately transported to the microwave chemical reactor and constantly stirred at 50 rpm. The microwave chemical reactor with varying output power (MP = 450, 720, and 900 W) was then switched on. Samples were removed (using a 3 mL syringe) at appropriate time intervals and immediately filtered through a 25 mm diameter 0.45 μm membrane filter. The adsorption of the dye on the filter membrane was found to be negligible. The sample temperature was measured using a thermometer, and the dye concentration was evaluated using UV–Vis spectrophotometry. In addition, the removal of Blue solution or Yellow solution using

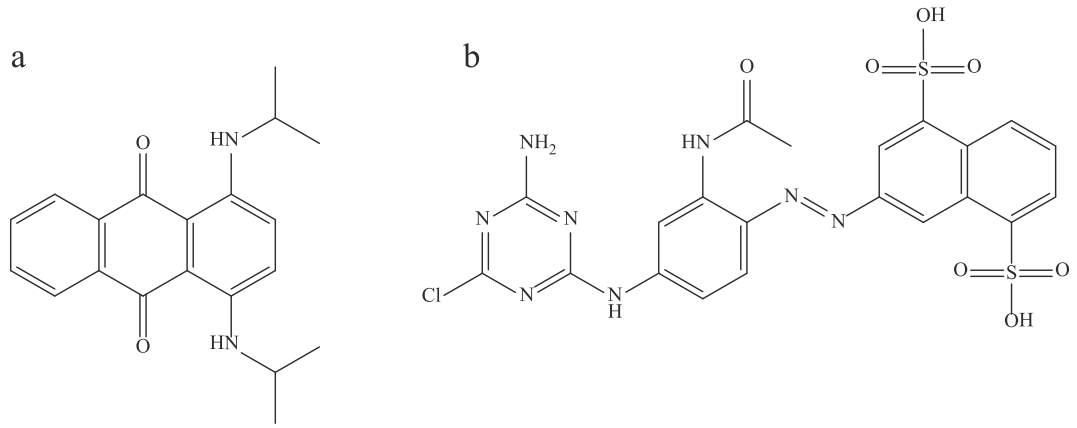

Fig. 1 – Molecular structures of Solvent Blue 36 (a) and Reactive Yellow K-RN (b).

only nZVI was performed for comparative purposes. To evaluate the effect of temperature on dye removal, we also carried out the reactions without MW in a thermostatic magnetic mixer (Yuhua Instrument, Gongyi, Henan, China) at different temperatures (25 and 70°C) controlled by a constant temperature bath; the samples were pipetted and treated in an identical manner to that described above.

1.4. Chemical analysis

The specific surface areas (BET surface area) of the dry nZVI particles were measured by the nitrogen adsorption method using an Autosorb-iQ surface analyzer (Quantachrome Instruments, Boynton Beach, Florida, USA). The morphology of the particles was observed with a Tecnal 20 U-twin (FEI, Hillsboro, Oregon State, USA) transmission electron microscope (TEM) at 120 kV to characterize the size and size-distribution of the metal particles. Elemental analysis of nZVI was conducted using a PW4400X-ray fluorescence (XRF, Thermo Electron Corporation, Waltham, Massachusetts, USA) spectrometer.

The concentration of dyes in the different samples was measured using a UV–Vis spectrophotometer (TU-1901, Persee, Beijing, China). From full wavelength scanning, it was found that the absorption maxima in the UV–Vis spectra of Blue solution and Yellow solution occur at 603 and 423 nm, respectively. Calibration curves (linear) for determining the dye concentrations were developed based on the absorbance signal measured using excess dye concentrations, giving rise to high r^2 values (>0.99).

Total organic carbon (TOC) of dye samples was tested by a TOC analyzer (Aurora 1030D, O.I., College Station, Texas, USA). Fe(II) concentrations in dye samples were determined spectrophotometrically using the ferrozine method (Gibbs, 1976). The concentration of total soluble Fe (Fe_T) in dye samples was quantified with an inductive coupled plasma emission spectrometer (OPTIMA 7000DV, PerkinElmer, Waltham, Massachusetts, USA).

2. Results

2.1. Characterization of nZVI

The BET surface area of nZVI was 15.7 m^3/g, and the average pore width and pore volume of agglomerated nZVI were 1.426 nm and 0.07 m^3/g, as determined using the Autosorb-iQ surface analyzer. The BET surface area of nZVI is half of the value (33.5 m^3/g) reported by Wang and Zhang (1997), but is consistent with the value (15.524 m^3/g) reported by Taha and Ibrahim (2014). A TEM image of the synthesized nZVI is shown in Fig. 2a, in which perfectly spherical, black nZVI particles *ca.* 40–70 nm in diameter can be observed; however, because the synthesized nZVI particles agglomerate when not used, an accurate measurement of the diameter of the individual particles was not possible in this study. Nevertheless, the diameter can be calculated to be 48.6 nm from the BET surface area using the equation from Taha and Ibrahim (2014), indicating the formation of smaller particles than previously reported (Joo et al., 2004; Wang and Zhang, 1997). The reduced size of the nZVI particles indicates that the presence of starch in the nZVI preparation process dispersed the nZVI particles in solution to give rise to smaller nZVI particles. Based on the XRF analysis of nZVI (Fig. 2b), the elemental composition of nZVI was determined to be 99.71% Fe and 0.134% Cl, indicating that a small amount of Cl^- ions in the solution was absorbed onto the nZVI during preparation. It should be noted that XRF could not be used to determine the presence of oxygen because of the low fluorescence quantum yield of light elements. Therefore, the elemental composition of nZVI determined from XRF may have some errors. However, it is believed that oxygen would be present in very small proportions because the production of nZVI was performed under anaerobic conditions.

2.2. Kinetics of dyes removal by nZVI and MW–nZVI

Typical calibration data for investigating the kinetics of dye removal are shown in Fig. 3. The efficiency of the dye removal using only nZVI increased gradually with increasing contact time. During the initial 15 min (first stage), the dyes were rapidly discolored with a high probability of the adsorption of organic molecules onto the nZVI surface and the reduction of the chromophoric group of the organic molecules in the aqueous phase. The reaction involving the dissolution of ferrous ions of nZVI and electron transfer has been proved to be a fast process in a previous study (Shu et al., 2007). After complete mixing of nZVI and the dye solution, most of the active surface of nZVI was occupied by dye molecules; thus, the reaction rate slowed down and approached equilibrium,

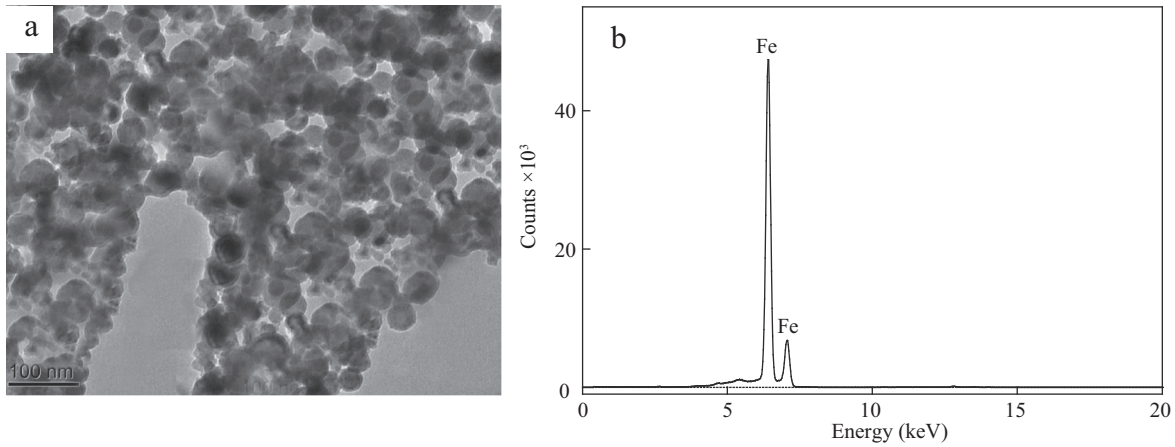

Fig. 2 – Transmission electron microscopy image (a) and X-ray fluorescence spectrum (b) of synthesized nanoscale zero-valent iron.

as observed for the last 15 min of the overall reaction time of 30 min. It is evident from Fig. 3 that nZVI was more effective for the removal of Blue than for Yellow, which is attributed primarily to the larger number of organic groups present in a molecule of Yellow compared to a molecule of Blue; thus, the former requires more nZVI to be degraded.

The use of MW radiation in combination with nZVI markedly increased the dye-removal rate and efficiency in both cases. When 50 mg/L Blue solution was subjected to treatment with MW–nZVI, as shown in Fig. 4, the maximum Blue removal efficiency achieved after 5 min was 56.5% and 81.4% using nZVI content (C_{Fe}) 0.1 and 0.2 g/L at pH 7.0 and MP 450 W, respectively. These values are respectively 21.1% and 19.9% higher than the dye-removal efficiency achieved with nZVI alone in 30 min. When the MP was increased from 450 to 900 W, the maximum removal efficiency increased from 56.5% to 66% for C_{Fe} = 0.1 g/L and from 80.9% to 90.2% for C_{Fe} = 0.2 g/L. The trends observed for the removal of Yellow with MW–nZVI (Fig. 5) were similar to those observed for Blue. Using C_{Fe} = 0.1 and 0.3 g/L, the maximum removal efficiencies of 60 mg/L Yellow were 40.4% and 64.8% at pH 7.0 and MP 450 W, which were achieved within 5 min, representing impressive enhancements of 27.3% and 28.9% relative to that achieved with only nZVI in 30 min. Furthermore, increasing the MP from 450 to 900 W could only enhance the removal efficiency of Yellow from 40.4% to 50.0% for C_{Fe} = 0.1 g/L and from 60.0% to 66.7% for C_{Fe} = 0.3 g/L. It was shown that the removal efficiency increased nonlinearly with increasing MP. Hence, the dominant factor influencing dye removal was the nZVI loading, whereas the MW primarily exerted an enhancement effect.

2.3. Effect of pH on dye removal by nZVI and MW–nZVI

The effect of pH on the dye removal efficiency was evaluated. The data in Fig. 3 show that increasing the pH resulted in a decrease in the removal efficiency for both Blue and Yellow. The maximum efficiency for removal for 50 mg/L Blue utilizing C_{Fe} = 0.2 g/L declined from 67.5% at pH = 5.0 to 48.9% at pH = 9.0, and the maximum efficiency for the

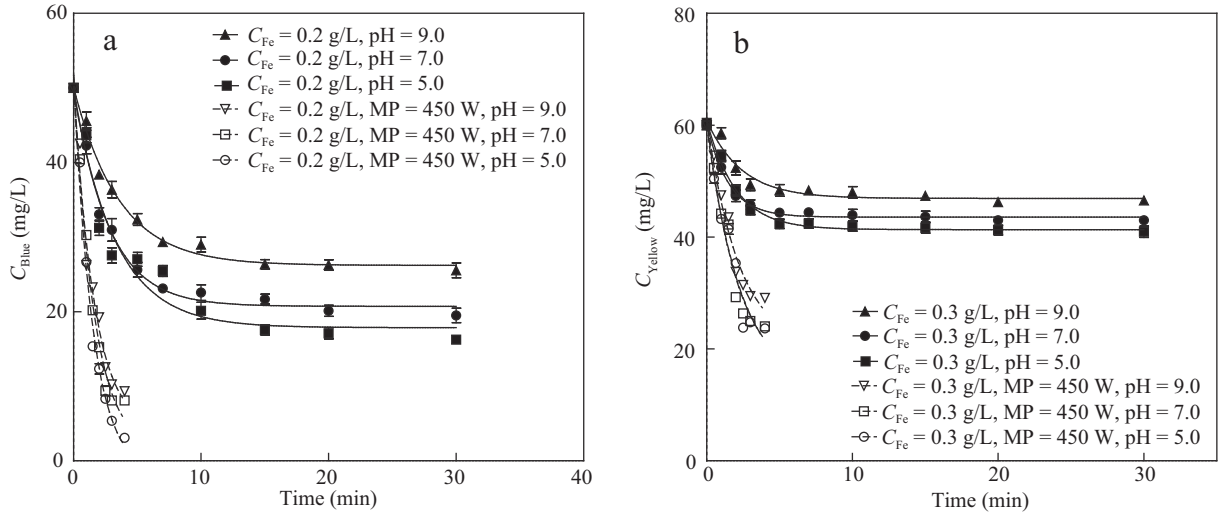

Fig. 3 – Nonlinear regression for kinetics of Solvent Blue 36 (Blue, a) and Reactive Yellow (Yellow, b) removal using only nanoscale zero-valent iron or microwave radiation in combination with nanoscale zero-valent iron.

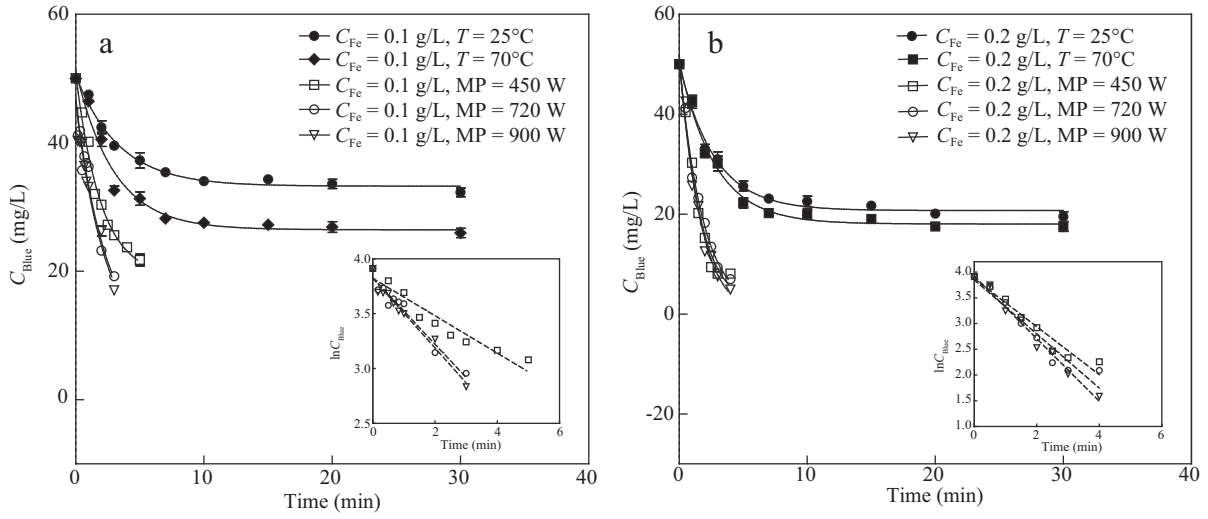

Fig. 4 – Nonlinear regression (solid lines) for kinetics of Blue removal using only nanoscale zero-valent iron at various temperatures at pH = 7.0 and using MW–nZVI at various microwave output power, C_{Fe} = 0.1 g/L (a) and 0.2 g/L (b) at pH = 7.0. Pseudo first-order model (dotted lines) for the kinetics of Blue removal by microwave radiation in combination with nanoscale zero-valent iron at pH = 7.0.

removal of 60 mg/L Yellow using C_{Fe} = 0.3 g/L decreased from 31.8% at pH = 5.0 to 22.9% at pH = 9.0. In addition to the effects of nZVI loading and MW power on dye removal, the effect of pH on the dye-removal efficiency was also investigated (Fig. 3). At MP = 450 W, the maximum removal efficiency of Blue using C_{Fe} = 0.2 g/L achieved in 5 min decreased from 93.8% at pH = 5.0 to 80.9% at pH = 9.0, and the maximum removal efficiency of Yellow using C_{Fe} = 0.3 g/L achieved in 5 min decreased from 59.9% at pH = 5.0 to 51.5% at pH = 9.0.

Increasing the pH was evidently an unfavorable factor for dye removal in this study, which is similar to the trend observed for Methyl Orange removal using nZVI (Fan et al., 2009) and for nitrate removal using nZVI (Yang and Lee, 2005). The faster corrosion of nZVI at lower pH leads to the generation of more hydroxyl radicals in the solution, with the consequent degradation of more dye molecules and higher dye-removal efficiency. Additionally, the point of zero charge of nZVI was determined to be 8.0 by Li et al. (2006); therefore, the surface of nZVI is positively charged at pH > 8.0, and can thus attract negatively charged amine groups in the dye molecules, leading to the better adsorption of the dyes on the surface of nZVI. At pH < 8.0, the surface of nZVI is negatively charged, which affects the adsorption of the dyes on its surface.

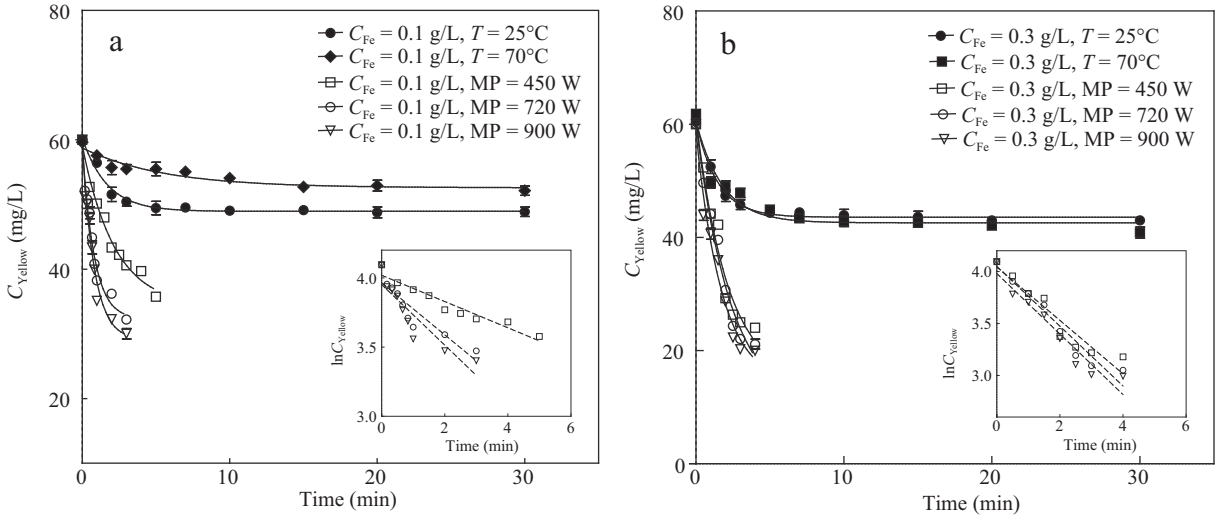

Fig. 5 – Nonlinear regression (solid lines) for kinetics of Yellow removal using only nanoscale zero-valent iron at various temperatures at pH = 7.0 and using (MW-nZVI) microwave radiation in combination with nanoscale zero-valent iron (MW-nZVI) at various microwave output power, C_{Fe} = 0.1 g/L (a) and 0.3 g/L (b) at pH = 7.0. Pseudo first-order model (dotted lines) for the kinetics of Yellow removal by MW–nZVI at pH = 7.0.

2.4. TOC removal by nZVI and MW–nZVI

The intermediates during dye degradation may have no contribution to the absorbance at the studied wavelengths, while TOC levels in the solutions can be used to qualify the amount of organics. Therefore, the removal efficiencies of TOC were simultaneously measured at varying pH. It can be seen in Fig. 6 that the maximum TOC removal efficiency by nZVI was 25.6% for Blue (20.3% for Yellow) after 30 min at pH 5.0, and the maximum TOC removal efficiency by MW–nZVI was 60.2% for Blue (41.5% for Yellow) after 5 min at pH = 5.0. It was evident in both cases that the use of MW radiation markedly increased the TOC efficiency (by *ca*. 25%) and the TOC removal efficiency was lower than the dye degradation efficiency (by *ca*. 20%). The results further indicated that the dyes were degraded in the nZVI or MW–nZVI systems by producing a number of intermediates prior to mineralization, and the use of MW radiation dramatically enhanced the mineralization efficiency.

2.5. Formation of iron species in nZVI and MW–nZVI systems

In the process of dye degradation by nZVI or MW–nZVI, iron species, including ferrous iron and ferric iron, can be formed *via* the two-electron transfer between nZVI and oxygen. To verify the mechanism of dye degradation, the concentrations of Fe(II) and Fe_T during the Blue removal were determined simultaneously. The concentration of Fe(II) in the system with C_{Fe} = 0.2 g/L was measured as 0.120, 0.013, and 0.008 mmol/L after 30 min at pH 5.0, 7.0, and 9.0, respectively, while the concentration of Fe(II) in the system with C_{Fe} = 0.2 g/L and MP = 450 W was markedly reduced to 0.082, 0.0017, and 0.0002 mmol/L after 5 min at pH 5.0, 7.0, and 9.0, respectively, indicating that the corrosion of nZVI was faster at lower pH and the reaction of Fe(II) with oxygen to produce Fe(III) and H_2O_2 in the presence of MW radiation was faster than that in the absence of MW radiation. However, the concentration of Fe_T had the opposite tendency after the use of MW radiation. The higher residual Fe_T at C_{Fe} = 0.2 g/L and MP = 450 W (0.242, 0.138 and 0.091 mmol/L after 5 min at pH 5.0, 7.0, and 9.0) compared to that at C_{Fe} = 0.2 g/L (0.154, 0.042 and 0.025 mmol/L after 5 min at pH 5.0, 7.0, and 9.0) was attributed to the fast corrosion of nZVI in the presence of MW radiation.

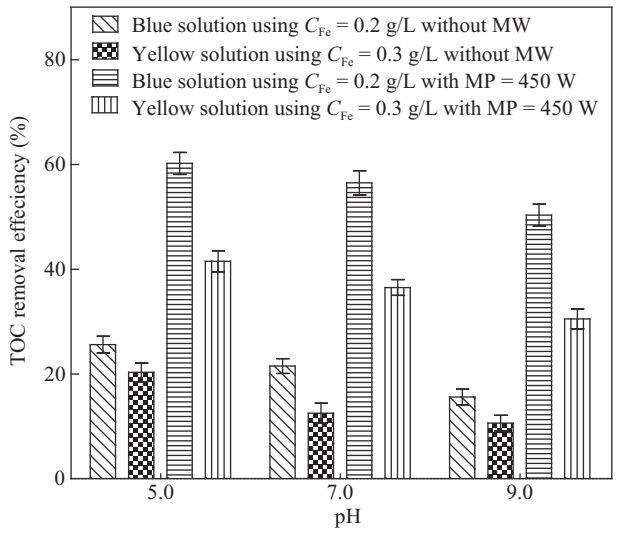

Fig. 6 – TOC removal efficiency of dye solutions using nanoscale zero-valent iron (nZVI) and microwave radiation in combination with nanoscale zero-valent iron at various pH levels.

3. Discussion

3.1. Kinetic model for dye removal by nZVI and MW–nZVI

To describe the kinetics of dye removal by nZVI and MW–nZVI, the following empirical equation was used (Shu et al., 2007):

$$C = (C_0 - C_e) \times \sigma \times e^{-k_e t} + C_e \quad (2)$$

where, C (mg/L) is the concentration of the dye at reaction time t, C_0 (mg/L) is the initial concentration of the dye, C_e (mg/L) is the concentration of the dye when the reaction reaches equilibrium, k_e (sec^{-1}) indicates the empirical rate constant for dye-removal kinetics, and σ denotes the variation coefficient, which was determined to be 1 by Fan et al. (2009).

The half-life ($t_{1/2}$, sec) of the dye can be expressed by the following equation:

$$t_{1/2} = \frac{\ln 2}{k}. \quad (3)$$

Using nonlinear regression, a summary of the constants obtained (C_e, k_e, and $t_{1/2}$) for dye degradation kinetics based on different experimental data is given in Table 1. The r^2 value ranged from 0.918 to 0.994, indicating good agreement between the empirical equation (Eq. (2)) and the observed data. The good fits of the kinetic models using different experimental variables are shown in Figs. 3–5. Variations of C_e with MP for different dyes and pH = 7.0 with different nZVI loadings are consistent with the experimental results demonstrating that MW radiation effectively enhanced the dye-removal efficiency, and that increasing the MP did not linearly increase the removal efficiency. Additionally, when more nZVI was loaded into the dye solutions, the enhancement in the dye-removal efficiency following MW radiation of the system was much higher. This result also indicated that, in this case, the dominant factor influencing the dye removal was nZVI, and MW radiation promoted dye removal by nZVI.

The kinetics of dye removal by MW–nZVI could be described using the pseudo first-order model (Figs. 4 and 5) with the r^2 value ranging from 0.829 to 0.984 (Table 2). The rate constants k_1 increased with increasing nZVI dosage and MW power, and with the same dosage of nZVI and MW power, the rate constants k_1 for Blue were higher than for Yellow. However, the kinetics of dye removal by nZVI without MW radiation did not comply with the pseudo first-order model (figures were not shown), which is consistent with studies by Yang and Lee (2005) and Wang et al. (2006) and inconsistent with studies from Nam and Tratnyek (2000), Bigg and Judd (2001), and Epolito et al (2008).

3.2. Role of MW radiation in dye removal

It was found herein that the combination of MW radiation and nZVI was useful for achieving higher dye decolorization efficiency in a shorter duration than that achieved with only

Table 1 – Parameters for empirical kinetics model.

Experimental variables						Empirical kinetics			
Dyes	C_{Fe} (g/L)	T (°C)	pH	Time (min)	MP (W)	C_e (mg/L)	k_e (sec^{-1})	$t_{1/2}$ (sec)	r^2
Blue	0.1	25	7.0	30	0	33.2	4.99×10^{-3}	139	0.986
	0.1	70	7.0	30	0	26.5	5.64×10^{-3}	122.8	0.974
	0.1	65	7.0	5	450	19.1	8.58×10^{-3}	80.8	0.987
	0.1	71	7.0	3	720	8.13	7.09×10^{-3}	97.7	0.935
	0.1	78	7.0	3	900	7.90	7.09×10^{-3}	94.8	0.951
	0.2	25	7.0	30	0	20.7	6.09×10^{-3}	113.8	0.991
	0.2	70	7.0	30	0	18.0	6.04×10^{-3}	114.8	0.990
	0.2	66	7.0	5	450	1.87	9.18×10^{-3}	75.5	0.986
	0.2	73	7.0	3	720	1.31	10.4×10^{-3}	66.9	0.985
	0.2	79	7.0	3	900	0.79	10.1×10^{-3}	69.0	0.981
	0.2	25	5.0	30	0	17.9	5.09×10^{-3}	136.2	0.954
	0.2	25	9.0	30	0	26.2	4.70×10^{-3}	147.6	0.990
	0.2	65	5.0	5	450	0.893	10.9×10^{-3}	63.5	0.989
	0.2	66	9.0	5	450	4.10	10.4×10^{-3}	66.9	0.985
Yellow	0.1	25	7.0	30	0	52.6	3.04×10^{-3}	228.1	0.918
	0.1	70	7.0	30	0	49.0	9.98×10^{-3}	69.5	0.979
	0.1	65	7.0	5	450	34.3	7.66×10^{-3}	90.5	0.983
	0.1	69	7.0	3	720	32.3	20.8×10^{-3}	33.4	0.972
	0.1	78	7.0	3	900	29.1	20.4×10^{-3}	34.0	0.971
	0.3	25	7.0	30	0	43.6	11.4×10^{-3}	61.1	0.994
	0.3	70	7.0	30	0	42.6	9.29×10^{-3}	74.6	0.941
	0.3	65	7.0	5	450	14.4	7.79×10^{-3}	89.0	0.962
	0.3	70	7.0	3	720	9.60	7.05×10^{-3}	98.3	0.980
	0.3	78	7.0	3	900	14.0	9.58×10^{-3}	72.4	0.973
	0.3	25	5.0	30	0	41.3	8.38×10^{-3}	82.7	0.990
	0.3	25	9.0	30	0	46.9	7.00×10^{-3}	147.6	0.947
	0.3	65	5.0	5	450	12.7	7.04×10^{-3}	98.5	0.957
	0.3	66	9.0	5	450	20.3	7.69×10^{-3}	90.2	0.969

C_{Fe}: nZVI content; T: temperature; MP: output power of microwave.

nZVI. The rapid, selective, and three-dimensional MW heating sharply elevated the temperature of the dye solutions with different nZVI loadings (Fig. 7), and the final temperature of the dye solutions was *ca.* 70°C (Table 1), indicating that the nZVI loading did not significantly affect the increase in the solution temperature. Nevertheless, it cannot be conclusively stated that nZVI was not a significant MW-absorbing material considering the small quantity of nZVI used in this study. It can only be deduced that the dominant MW-absorbing material in this system was water. To investigate the effect of temperature on dye removal by nZVI, several experiments were performed at different temperatures (25 and 70°C) in a thermostatic magnetic mixer (Figs. 4 and 5). Although the dye-removal efficiency increased slightly with temperature, this increase was far less than the efficiency achieved with MW thermal radiation. This implies that the rapid and selective heating of the dispersant (water in this case) by MW radiation was not the dominant mechanism for dye removal, which was consistent with the research by Horikoshi and Serpone (2014). Previous studies (Horikoshi et al., 2004a; Jones et al., 2002; Liu et al., 2004; Lü et al., 2009) showed that hot spots were induced in the solutions when MW-absorbing materials such as activated carbon and TiO_2 were added to the MW medium. These hot spots may not induce an apparent increase in the temperature but may produce analogous plasmas around the hot spots (Horikoshi et al., 2004a), accelerating the degradation of target pollutants (Horikoshi et al., 2002). Meanwhile, although the quantized energy of MW radiation (10^{-6}–10^{-3} eV), which is much less than that of a chemical bond (10^{0}–10^{1} eV), cannot directly induce breakage of the chemical bonds (Müller et al., 2003), MW radiation can cause vibration or rotation of the chemical bonds, and hence weaken them and reduce the activation energy during the reaction with nZVI. Another possible explanation is that MW radiation may disrupt the hydrogen bonding of water molecules, thus activating them and promoting the desorption of water molecules from the surface of nZVI, increasing the surface activity of nZVI toward dye molecules. It was also revealed that the use of MW radiation could accelerate the corrosion of nZVI and the reaction of Fe(II) with oxygen to

Table 2 – Parameters of pseudofirst-order model for dye removal by microwave radiation in combination with nanoscale zero-valent iron at pH = 7.0.

C_{Fe} (g/L)	Blue						Yellow					
	0.1			0.2			0.1			0.3		
$k_1 \times 10^{-3}$ (sec^{-1})	2.84	5.04	5.29	7.78	8.76	10.1	1.58	3.13	3.65	4.28	4.79	4.85
r^2	0.920	0.954	0.970	0.946	0.927	0.984	0.929	0.836	0.829	0.910	0.946	0.928

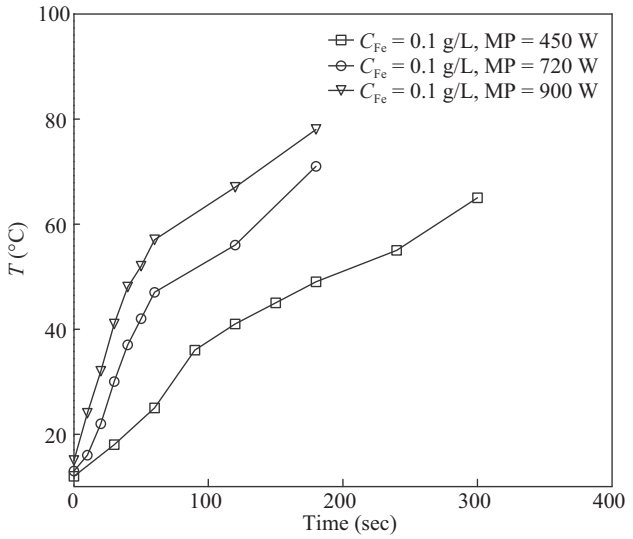

Fig. 7 – Elevated temperature curve for Blue removal by C_{Fe} = 0.1 g/L and different output power of microwave (450 W, 720 W and 900 W) at pH = 7.0.

produce the Fe(III) and H_2O_2, and enhance the degradation of dyes as a consequence.

4. Conclusions

The rapid and effective removal of dyes (Solvent Blue 36 and Reactive Yellow K-RN) by MW–nZVI under different experimental conditions was demonstrated herein. MW radiation significantly enhanced the degradation of the dyes and the mineralization efficiency in the presence of nZVI in 5 min. Increasing the pH decreased the efficiency of dye removal in the presence of both nZVI as well as with MW–nZVI; however, the dye-removal efficiency did not increase linearly in response to MP. Both the kinetics of dye removal by nZVI and by MW–nZVI could be described by an empirical equation. However, the pseudo-first-order model was only suitable for the kinetics of dye removal by MW–nZVI.

Although it has been concluded that the multiple actions of MW radiation may be the reaction mechanism for dye removal (as determined by eliminating the effect of rapid and selective heating of MW radiation on dye removal and accelerating the reaction of Fe(II) with oxygen to produce the Fe(III) and H_2O_2), the pathways for the degradation of dyes and a detailed understanding of the reactions between the dyes and nZVI under MW radiation were not elucidated in this study. These studies are currently underway and will be reported in a future paper.

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