

Decolorization of Reactive Black 5 and Reactive Red 198 using nanoscale zerovalent iron

C. Chompuchan, T. Satapanajaru, P. Suntornchot, and P. Pengthamkeerati

Abstract— Residual dye contents in textile dyeing wastewater have complex aromatic structures that are resistant to degrade in biological wastewater treatment. The objectives of this study were to determine the effectiveness of nanoscale zerovalent iron (NZVI) to decolorize Reactive Black 5 (RB5) and Reactive Red 198 (RR198) in synthesized wastewater and to investigate the effects of the iron particle size, iron dosage and solution pHs on the destruction of RB5 and RR198. Synthesized NZVI was confirmed by transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The removal kinetic rates (k_{obs}) of RB5 (0.0109 min^{-1}) and RR198 (0.0111 min^{-1}) by 0.5% NZVI were many times higher than those of microscale zerovalent iron (ZVI) (0.0007 min^{-1} and 0.0008 min^{-1} , respectively). The iron dosage increment exponentially increased the removal efficiencies of both RB5 and RR198. Additionally, lowering pH from 9 to 5 increased the decolorization kinetic rates of both RB5 and RR198 by NZVI. The destruction of azo bond (N=N) in the chromophore of both reactive dyes led to decolorization of dye solutions.

Keywords— decolorization, nanoscale zerovalent iron, Reactive Black 5, Reactive Red 198

I. INTRODUCTION

THE effluent discharged from textile dyeing mill results in high concentrated color wastewater and consists of various types of color. Most dyestuffs are complex aromatic structures which are difficult to be disposed. Moreover, the colors in water resources pose aesthetic problem. They also cause serious ecological problems for example, they significantly affects photosynthetic activity of aquatic plants due to reduced light penetration and may be toxic to some aquatic organism [1].

Nowadays, there are many methods for dye removal such as chemical coagulation, flocculation, chemical oxidation, photochemical degradation, membrane filtration, aerobic and anaerobic biological degradation. All of these methods suffer from one or other limitations, and none of them are successful in completely removing the colors from wastewater [2].

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Over the last decade, nanotechnology represents a new generation of environmental technology that provides high effectiveness solutions to environmental cleanup and remediation by using nanoscale zerovalent iron (NZVI) (particle size 1-100 nm) as chemical reductant [3]. The high effectiveness of NZVI was due to its high surface area and surface reactivity which higher than microscale zerovalent iron (ZVI) about 10 – 10,000 times. Previous laboratory studies indicated that NZVI was effective for the transformation of various environmental contaminants and it also enhanced their biodegradability such as chlorinated organic solvents [4], organochlorine pesticides [5], and PCBs [6]. In spite of the successful transformation of the contaminants by NZVI, less research has been conducted on dye removal applications [7-8].

The objectives of this study were to determine the effectiveness of nanoscale zerovalent iron (NZVI) to decolorize Reactive Black 5 (RB5) and Reactive Red 198 (RR198) in synthesized wastewater and to investigate the effects of the iron particle size, iron dosage and solution pH on the destruction of RB5 and RR198.

II. MATERIALS AND METHODS

A. Materials

Reactive Black 5 (RB5) and Reactive Red 198 (RR198) were obtained from Thongthai Textile Co., Ltd., Thailand. The chemical structures are illustrated in Fig. 1.

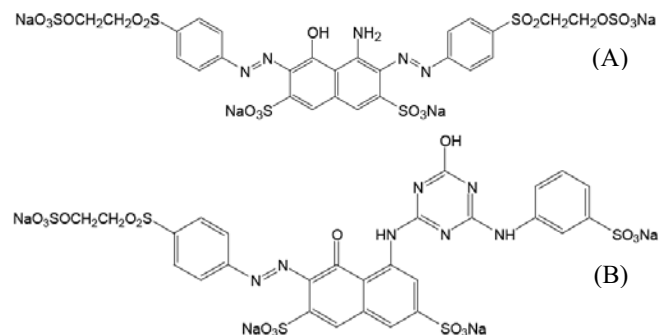
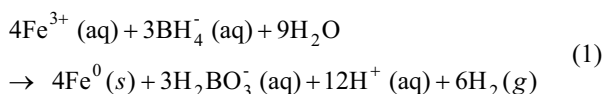


Fig. 1 Reactive Black 5 (A) and Reactive Red 198 (B)

Commercial ZVI powder (purity 99%) was purchased from S.D. Fine Chem Limited (particle size 100 mesh). Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was obtained from Ajax. Sodium borohydride (NaBH_4) was purchased from Asia Pacific Specialty Chemicals Limited. Hydrochloric acid (HCl) was purchased from J.T. Baker. Sodium hydroxide (NaOH) was purchased from Carlo Erba Reagents. Methanol was purchased from Merck.

B. Preparation of nanoscale zerovalent iron

Synthesis of nanoscale iron particles was achieved by adding 1:1 volume ratio of NaBH_4 (0.25 M) into $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.045 M) [4]. The solutions were mixed under room temperature ($30 \pm 1^\circ\text{C}$) for 5 minutes. Ferric iron was reduced by borohydride according to the following equation:



The iron particles formed by this reaction were washed by deionized water and then were washed with methanol to prevent immediate rusting. The synthesized iron particles were separated from the solution using magnet and dried by N_2 gas.

C. Characterizations of ZVI and NZVI

Specific surface areas of the ZVI and NZVI particles were determined by BET method using Quantachrome: Autosorb-1. Size and shape of the iron particles were studied by Transmission Electron microscope (TEM) JEOL: JEM1220. X-ray diffractometer (XRD) Philips X'Pert was used to investigate the material structure of iron nanoparticles. X-ray photoelectron spectroscope (XPS) Shimadzu: Amicus Maker was used to determine the surface composition to a depth of less than 10 nm from the surface of iron nanoparticle.

D. Batch experiments

Batch experiments were conducted to compare the efficiencies of ZVI and NZVI to decolorize RB5 and RR198 in aqueous solution. Dye solutions were prepared in deionized water at initial concentration of 100 mgL^{-1} of RB5 or RR198. The 100 ml of dye solution was moved to 250 mL Erlenmeyer flask and then 0.25% or 0.5% (w/v) of ZVI or NZVI was added. The flask was stirred at 150 rpm by shaker. The experiment was performed in triplicate and conducted at room temperature. Samples were collected in at 0, 15, 30, 45, 60, 90, 120 and 180 minutes. The samples were centrifuged at 6,000 rpm for 5 minutes. The residual concentrations of dye were quantified by UV/VIS 918 spectrophotometer at 598 nm and 518 nm for RB5 and RR198, respectively. The RB5 and RR198 before and after treatment by NZVI were also qualified by observing the changes of UV/VIS spectrum. To investigate the effect of initial pH on decolorization of RB5 and RR198 by NZVI, the dye solution were adjusted pH at 5, 6, 7, 8, and 9 using HCl 1.0 M and NaOH 1.0 M before treatment by NZVI.

III. RESULTS AND DISCUSSIONS

A. Characterizations of ZVI and NZVI

The BET surface areas of the ZVI and NZVI were 2.55 and $29.67 \text{ m}^2\text{g}^{-1}$, respectively. TEM image of the NZVI particles is shown in Fig. 2. The laboratory prepared iron particles were round shape. The TEM image also shows that most particles were less than 100 nm and formed chain-like aggregates. The X-ray diffractograms of ZVI and NZVI (Fig. 3) reveal an apparent peaks at the same 2θ indicating the presence of micro scale zerovalent iron (Fe^0). The lower intensity was found in the NZVI sample, it may be due to its small particles that have less X-ray reflected area [9].

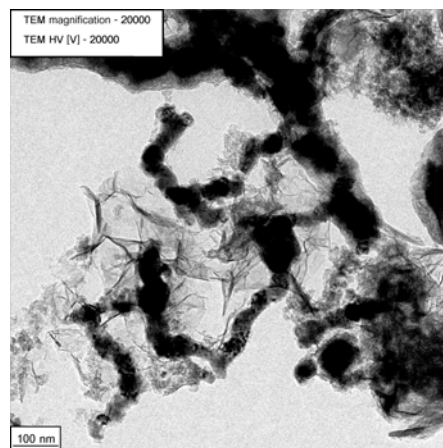


Fig. 2 TEM image of NZVI

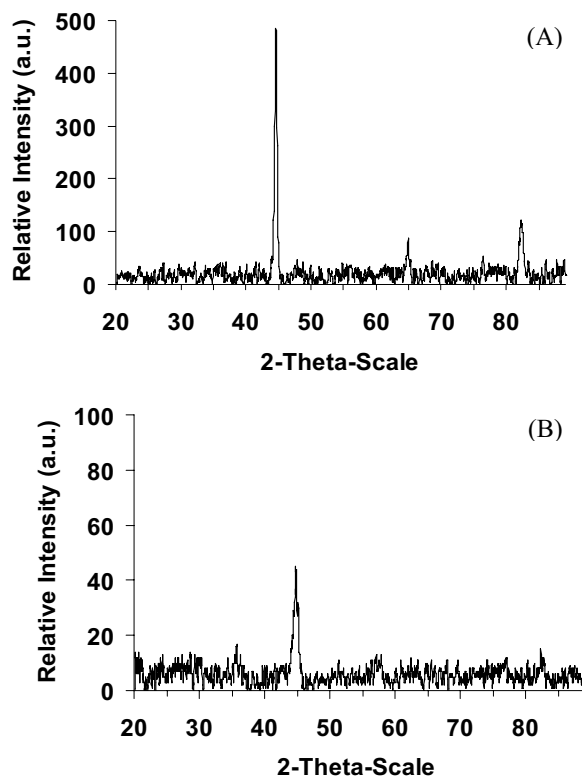


Fig. 3 X-ray diffractograms of ZVI (A) and NZVI (B)

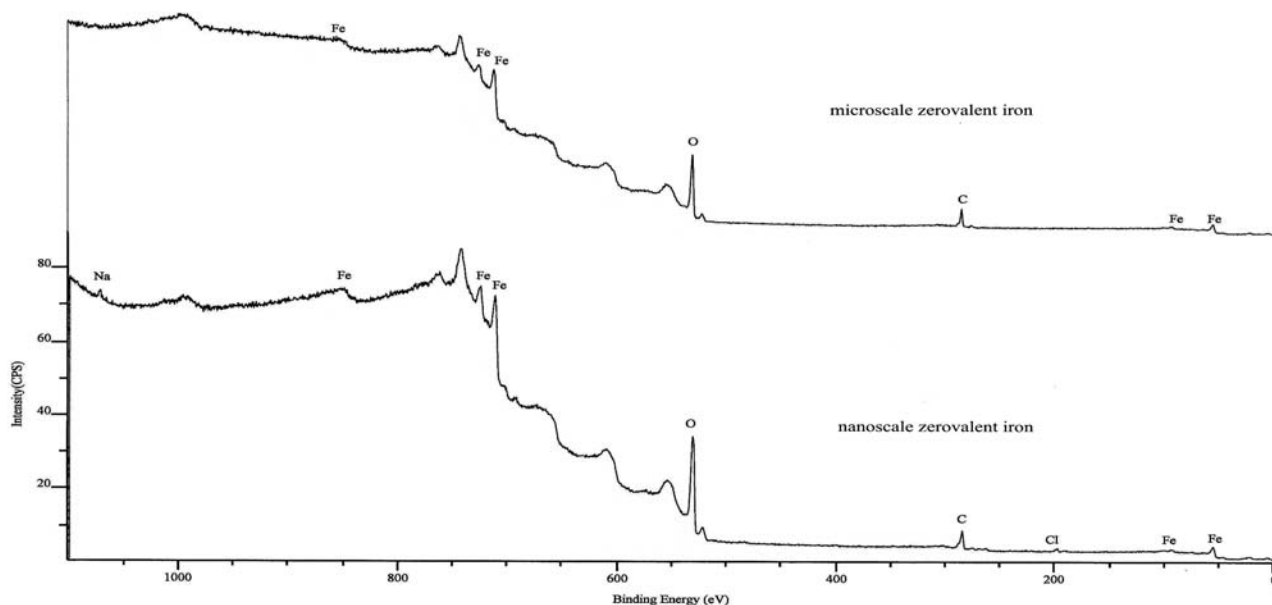


Fig. 4 XPS responses of ZVI and NZVI

XPS responses identify that surface of synthesized NZVI consisted of the Fe composition as same as the ZVI surface (Fig. 4). Small amount of sodium and chlorine were also detected on the NZVI surface. Therefore, results from XRD and XPS analysis indicated that the laboratory prepared NZVI particles were Fe⁰.

B. Decolorizations of RB5 and RR198 by ZVI and NZVI

Fig. 5 illustrates that the removal efficiencies of RB5 and RR198 by NZVI were much faster than those of ZVI under the same experimental conditions. This may have resulted from the higher surface area of NZVI versus ZVI which provided more iron surface active sites for collision with dye molecules to accelerate the dye removal efficiencies.

Correlation analyzes showed that the decolorization of the

both dyes were pseudo-first order reaction ($R^2 > 0.94$ for RB5 and RR198). Removal kinetic rate (k_{obs}) of RB5 and RR198 by NZVI were many times higher than those of ZVI. The decolorization kinetic rate constants show in Table I.

To compare the removal kinetic rate for Fe⁰, k_{obs} were normalized to the particles surface area. The rate of decolorization for dye in a batch system is described by the following equation [10]:

$$\ln[C(t)/C_0] = -k_{SA, dye} \rho_a t \quad (2)$$

Where $C(t)$ is the dye concentration (mgL^{-1}), C_0 is the initial dye concentration (mgL^{-1}), $k_{SA, dye}$ is the surface normalized reaction rate or the specific reaction rate, ($\text{Lm}^{-2}\text{h}^{-1}$), ρ_a is the

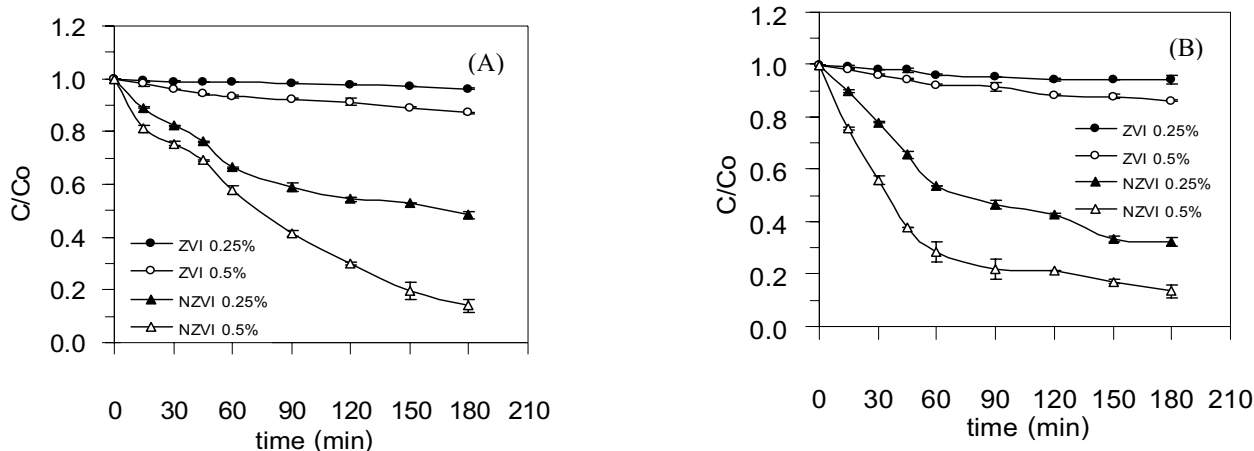


Fig. 5 Removals of RB5 (A) and RR198 (B) by ZVI and NZVI

specific surface area concentration of iron in the solution (m^2L^{-1}), and t is time (h). The specific reaction rate (k_{SA}) can be estimated from the value of the observation rate (k_{obs}) divided by the specific surface area concentration (ρ_a). The k_{SA} values for the decolorizations of RB5 and RR198 by ZVI and NZVI are shown in Table I.

TABLE I
REMOVAL KINETIC RATES (k_{obs}) AND SPECIFIC CONSTANT RATES (k_{SA})
FOR DECOLORIZATIONS OF RB5 AND RR198 BY ZVI AND NZVI

Iron, % (w/v)		Removal kinetic rate, k_{obs} (min^{-1})		Specific reaction rate, k_{SA} ($\text{Lm}^{-2}\text{h}^{-1}$)	
		RB5	RR198	RB5	RR198
0.25	ZVI	0.0002	0.0004	1.9×10^{-3}	3.8×10^{-3}
	NZVI	0.0040	0.0065	3.2×10^{-3}	5.2×10^{-3}
0.5	ZVI	0.0007	0.0008	3.4×10^{-3}	3.8×10^{-3}
	NZVI	0.0109	0.0111	4.4×10^{-3}	4.9×10^{-3}

From Table I, k_{SA} of the NZVI particles were higher than the ZVI particles. Wang and Zhang (1997) [6] reported k_{SA} for synthesized nanoscale iron particles toward PCE degradation was $3.0 \times 10^{-3} \text{ Lm}^{-2}\text{h}^{-1}$ which was higher than k_{SA} for commercially available iron particles (generally below $1.0 \times 10^{-3} \text{ Lm}^{-2}\text{h}^{-1}$). Providing more surface active sites in NZVI will accelerate color removal efficiencies of dyes [11]. In conclusion, the higher specific surface area, the higher surface reactivity to decolorize RB5 and RR198 by ZVI and NZVI. Additionally, the iron dosage increment exponentially increased the removal efficiencies of both RB5 and RR198.

C. The UV/VIS spectra of dye solutions before and after decolorization by NZVI

The absorbance peaks of the RB5 and RR198 in the visible region (400-700 nm) were disappeared after treatment by NZVI (Fig.6). The absorbance decreasing indicated that chromophore group, the basic functional group of dyes for its visible color, was broken down. Many previous experiments demonstrated that azo bond ($\text{N}=\text{N}$) was destroyed by zerovalent iron such as Acid Orange 2 [12], Reactive Black 8, [13] and Acid Blue 113 [14]. Most experiments revealed that the absorbance caused by the azo group became lower after treatment by zerovalent iron and the new absorbance of amino group appeared in UV/VIS chromatograph instead [12]. Feng, *et al.* (2000) [13] used GC/MS technique to investigate degradation products of Reactive Red 2 by the zerovalent iron. Their results confirmed that the azo linkage of Reactive Red 2 was reduced to hydrogenated azo structure without destroying benzene ring and naphthalene ring. Consequently, we can imply that the destruction of azo bond ($\text{N}=\text{N}$) of RB5 and RR198 by NZVI led to decolorization of dye solutions.

D. The effect of pH on dye decolorizations by NZVI

Removal efficiencies of RB5 and RR198 by NZVI at

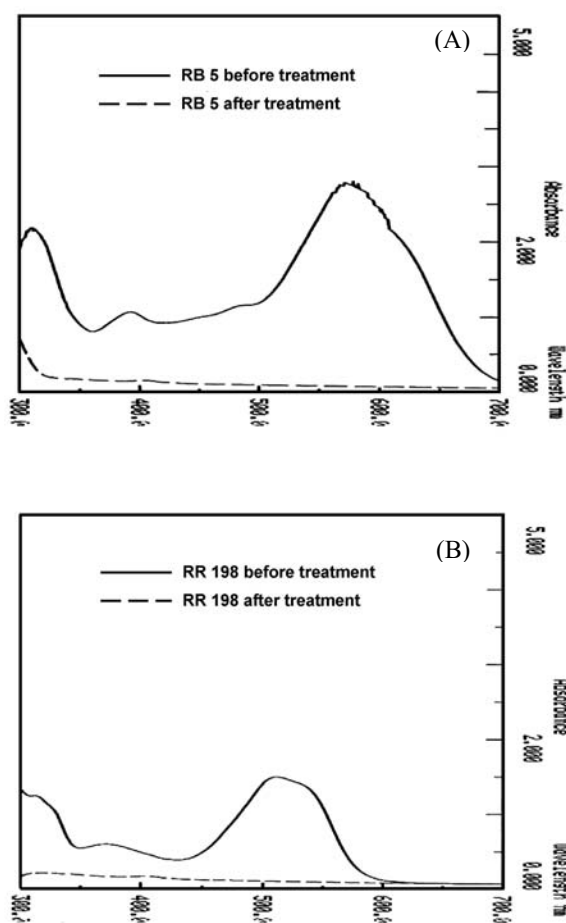


Fig. 6 UV/VIS spectra of RB5 (A) and RR198 (B) before and after decolorization by NZVI

various pHs are shown in Fig 7. The removal kinetic rate constants (k_{obs}) of the both dyes are also shown in Table II. From the results, lowering pH from 9 to 5 increased the removal kinetic rates. At pH 5, the decolorization efficiencies of both dyes were reached 100% after 120 minutes treatment. Similarly, Chang, *et al.* (2006) [11] reported that reducing pH to 2.1, 3.0, and 4.0 for Acid Black 24 removals using synthesized nanoscale zerovalent iron particles by addition of hydrochloric acid (1.0 molL^{-1}) resulted in the significant elevation of decolorization to more than 46.5% of the original pH (pH 6.4). Whereas, elevating the pH to 9.0, 10.2, and 10.9 by addition of sodium hydroxide solution (1.0 molL^{-1}) to dye wastewater with original pH of 6.4 resulted in lower decolorization efficiencies.

At high pH, the ferrous ions dissolved from the iron surface were collided with hydroxyl ions in alkaline solution, and ferrous hydroxides were produced and precipitated on the iron surface which led to occupy the reactive sites to hinder the reaction. [7]. Additionally, Zhang, *et al.* (2005) [15] reported that the degradation of Acid Orange 2 using Fe^0 occurred on the surface of metal iron when effective collision between dye molecules and elemental iron happened. Fe^0 , as an electron

donor, loses electrons while the dye molecule, as an electron acceptor, gets electrons and combines with H^+ and turns into transitional products and finally terminal products. As a consequence, pH would strongly affect the degradations of RB5 and RR198 by NZVI.

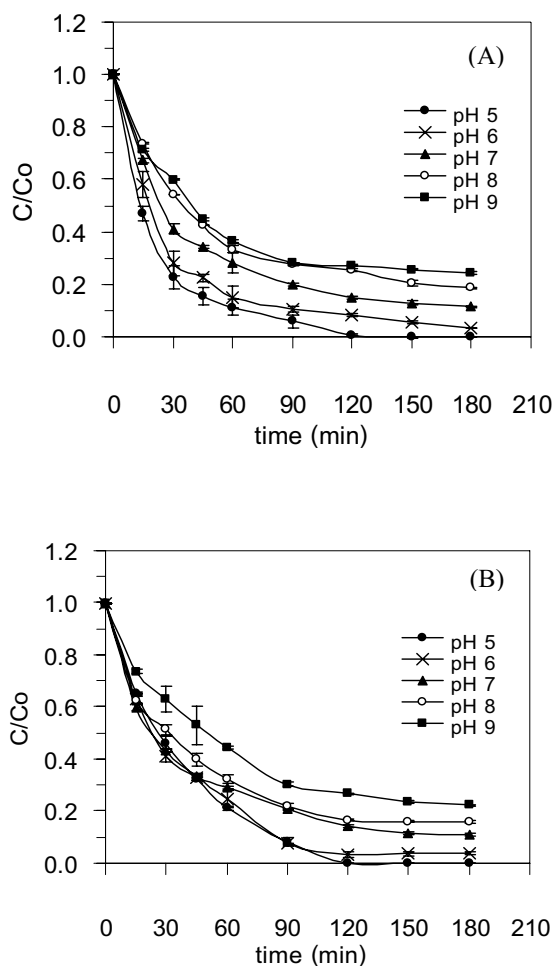


Fig. 7 The effect of pH on removals of RB5 (A) and RR198 (B) by ZVI and NZVI

TABLE II
REMOVAL KINETIC RATES (k_{obs}) FOR THE EFFECT OF pH ON
REMOVALS OF RB5 AND RR198 BY ZVI AND NZVI

Iron, % (w/v)		Removal kinetic rate, k_{obs} (min^{-1})	
		RB5	RR198
0.25	ZVI	0.0074	0.0083
	NZVI	0.0088	0.0101
0.5	ZVI	0.0114	0.0117
	NZVI	0.0169	0.0204

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