



Application of Synthesized Nanoscale Zero-Valent Iron in the Treatment of Dye Solution Containing Basic Yellow 28

T. Poursaberi¹, M. Hassanisadi^{1*}, F. Nourmohammadian²

¹. Assistant Professor, Department of Instrumental analysis, Research institute of petroleum industry, P.O.Box: 14665-137, Tehran, Iran.

². Associate Professor, (a) Center of Excellence for Color Science and Technology and (b) Department of Organic Colorants Research, Institute for Color Science and Technology, P.O.Box: 16765-654, Tehran, Iran.

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ABSTRACT

Nanoscale zero-valent iron (NZVI) particles were synthesized by the aqueous phase borohydride reduction method, and the synthesized NZVI particles were used for the degradation of Basic Yellow 28 (BY28) dye in aqueous solution. The influence of experimental variables such as reaction time, NZVI particle dosage and pH were studied on the decolorization of BY28. Mixing an aqueous solution of 100 mg L⁻¹ BY28 with 2 g L⁻¹ Fe⁰ resulted in 98.2% loss of BY28 within 15 min. The color removal efficiency was found to be increased with decrease in initial pH of dye solution and NZVI exhibited good color removal efficiency at acidic pH. Solvent extraction of the Fe⁰ revealed that BY28 removal was not through adsorption, but through degradation, as Fe⁰ treatment of BY28 lead to new chromatographic peaks (degradation products) in HPLC analysis. Prog. Color Colorants Coat. 5(2012), 35-40. © Institute for Color Science and Technology.

1. Introduction

Dye makes our world beautiful, but it brings us pollution. The pollution induced by dyestuff losses and discharge during dyeing and finishing processes in the textile industry has been a serious environmental problem for years. In addition, dye molecules are very visible in wastewaters due to their strong color at very low concentrations and as a consequence, the color is one of the most obvious indicators of water pollution. Dyes in the wastewater undergo chemical as well as biological changes, consume dissolved oxygen from the stream, and destroy aquatic life because of their toxicity [1]. This has

motivated many studies in the last decade toward the development of new processes for the removal of color and organic load from the contaminated effluents. The treatment of colored wastewater is commonly carried out using biological [2-5], physico-chemical methods such as oxidation, froth flotation and coagulation [6-9], adsorption [10-12] and electrochemical techniques [13-15]. Among these methods, one technology which has gained widespread acceptance is the use of zerovalent metals for remediating contaminated water.

Nowadays, the versatility of nanometer-scale zero-valent iron (NZVI), Fe⁰, has been demonstrated for potential use in environmental engineering [16] and over

*Corresponding author: mhsaadi@ripi.ir

the last few years, NZVI has been extensively used in the degradation of toxic and hazardous organic pollutants [17-19]. NZVI in the form of powder is a strong reducer, and it is cheap, easy to get and the spent iron particles could readily be recycled by a magnet [20]. In addition, a wide variety of reducible contaminants including chlorinated organic compounds, heavy metal ions and oxo-anions could be treated. Dyes are another category of complex chemicals that may be labile to reduction by Fe^0 , as has recently been shown for several azo dyes. While many of the commercially used dyes resist to biodegradation, the products (aromatic amine) of dye wastewaters decolorization by Fe^0 are easily degraded by microorganisms. The practical applicability of these NZVI particles lies in the fact that they reduce organic as well as inorganic impurities in order to get oxidized into +2 and +3 oxidation states [21].

In particular, the Basic Yellow 28 dye (BY28) is among the most commonly used dyestuffs to dye cotton and polyacrylonitrile, and is therefore a common industrial pollutant. BY28 is a cationic dye which can also called azomethin dye (-CH=N-) or hydrazone dye (=N-N (H,R)-). Generally textile effluents have a complex and variable composition, but the use of a simulated waste by means of an artificial aqueous solution facilitates the assessment of a treatment process. The goal of this study is to investigate the application of laboratory-synthesized NZVI for the decolorization of BY28 from contaminated wastewater and the analysis of the treated solution by HPLC to follow the quenching of the color and the formation of uncolored breakdown product.

2. Experimental

2.1. Reagents and chemicals

BY28 (Figure 1) was obtained from "Institute for Color Science and Technology, Tehran, Iran" with molecular weight of 433.52 g/mol and characteristic wavelength $\lambda_{\text{max}} = 438$ nm. The chemical reagents used in the study ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2SO_4 , NaOH , and NaBH_4) were reagent grade obtained from Aldrich Chemical Co. All other reagents were of analytical reagent grade. Deionized water was used throughout this study.

2.2. Equipments

Phillips EM 400ST transmission electron microscope (TEM) was used to characterize the Morphology and the distribution of the iron particles.

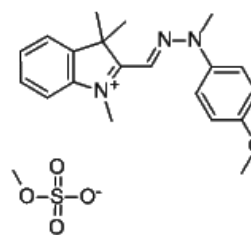


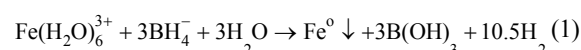
Figure 1: Chemical structure of BY28.

Powder X-ray diffraction (XRD) patterns of the solid products were obtained in the 2θ range of 5° - 80° using a PW-1840 diffractometer from Philips Co. with Cu-K α radiation ($\lambda=1.54178 \text{ \AA}$).

pH measurements were performed with a Metrohm 691 pH meter. The BY28 concentration was measured by double-wavelength absorbance (572 nm) by a Carry 5030 spectrophotometer from Varian Co. HPLC analysis were carried out using an Agilent HPLC chromatograph consists of UV/VIS detector (model 1200) with wavelength in the range of 190-800 nm and C18 $4\mu\text{m} \times 3.99 \text{ mm} \times 300\text{mm}$ column.

2.3. NZVI Synthesis

The NZVI material was synthesized by dropwise addition of 1.6 M NaBH_4 aqueous solution to a Ne gas-purged 1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution at room temperature with magnetic stirring as described by Wang and Zhang [22]. Ferric iron (Fe^{3+}) was reduced and precipitate according to the reaction 1:



The solution was stirred for 20 min and centrifuged at 6000 rpm for 2 min, and the supernatant solution was replaced by acetone. Acetone-washing prevented the NZVI from immediate rusting during purification leading to a fine black powder product after freeze-drying. All Fe materials were stored in a N_2 -purged desiccator.

2.4. Batch experiment

Batch experiments were performed in 100 mL flask. For each experiment, $0.5\text{-}3 \text{ gL}^{-1}$ NZVI particles were added to 50 ml BY28 solution (100 mgL^{-1} in deionized water) prepurged with N_2 for 5min. At 5, 10, 15, 20, 25 and 30 min, 5 mL aliquot was removed with syringe and filtered

through 0.45µm membrane filter, and the residual BY28 concentration in the solution (mgL⁻¹) was analyzed using a UV-VIS spectrum. The intermediates of BY28 degradation by Fe⁰ were analyzed by employing a HPLC.

Reactions proceeded for 30 min. Then, the BY28-treated NZVI was separated and gently washed with water and then was agitated for 1 h with 20 mL methanol. Aliquots of supernatant solution were filtered (0.45 µm) and analyzed for adsorbed BY28 by UV-VIS.

3. Result and discussion

3.1. Characterization of NZVI: Structure and particle size determination by TEM and XRD

Figure 2 shows the images of NZVI nanoparticles observed by transmission electron microscopy. It indicates that iron particles have a nearly spherical shape with a grain size range about 20- 50 nm. Figure 3 shows the XRD spectrum of NZVI nanoparticles. The main reflection at 44.7° corresponding to Fe⁰.

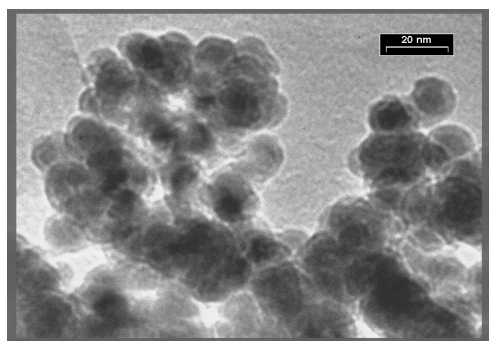


Figure 2: The TEM image of NZVI nanoparticles.

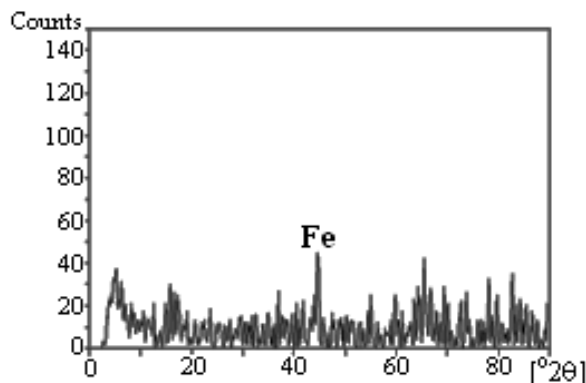


Figure 3: XRD spectrum of NZVI nanoparticles.

3.2. Effect of NZVI dosage

Experiments of BY28 removal with Fe⁰ were performed at an initial concentration of 100 mg L⁻¹. In Figure 4, the results of BY28 removal are shown using different Fe⁰ concentrations in the range of 1-5 gL⁻¹. There was an exponential decrease in the concentrations of BY28 in contact with Fe⁰ with increasing time. The results revealed that increasing the Fe⁰ concentration increased the amount of removed BY28. Maximum BY28 loss (98.2% within 15 min) occurred in the presence of 2 gL⁻¹ Fe⁰, while only 14.7% BY28 loss occurred during the first 15 min when 0.5 gL⁻¹ Fe⁰ was used.

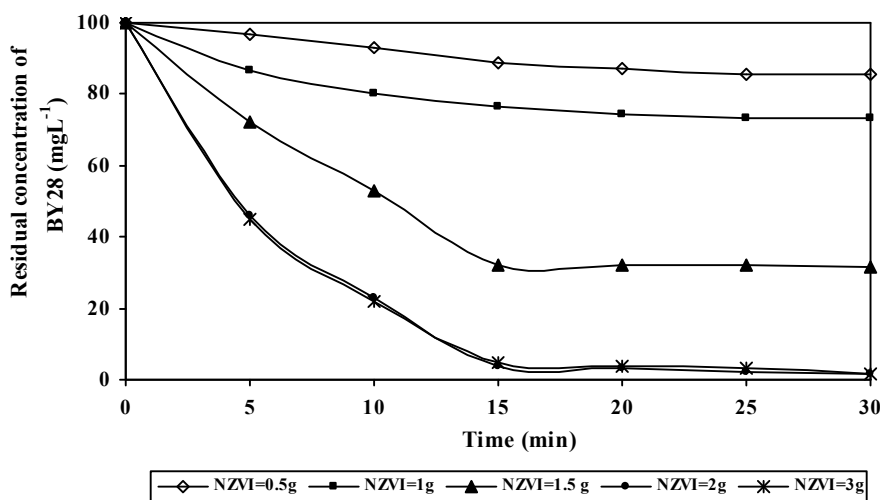


Figure 4: BY28 residual concentration versus time: initial BY28 concentration: 100 mgL⁻¹ with various NZVI dosages.

This is because more NZVI particles are able to provide more iron surface-active sites for collision with BY28 molecules to accelerate the BY28 removal efficiencies.

Thus, the BY28 removal efficiencies were gradually swelling from 14.7, 26.5, 68.3, to 98.2% by raising NZVI dosage from 0.5, 1, 1.5, to 2 g L⁻¹ as shown in Figure 4. Results show that 2 g L⁻¹ is an optimal amount of NZVI, beyond which no improvement of removal was obtained.

3.3. Effect of pH

The pH was also one of the important factors in the BY28 removal by zerovalent iron. When the ferrous ions dissolved from the iron surface, collided with hydroxyl ions in alkaline solution and precipitation of produced ferrous hydroxide on the iron surface occupy the reactive sites to hinder the reaction [23]. Also, lower pH gives rise to a greater extent of acid washing of iron oxides on metallic iron surfaces and reduces passivation of metal by enhancing solubility of metal hydroxide [24]. So, the chemical reduction of BY28 by NZVI is favorable in acid conditions.

The pH effect on BY28 removal is illustrated in Figure 5 (NZVI dosage: 2 g L⁻¹ and BY28 concentration: 100 mg L⁻¹). By comparing the removal efficiencies of BY28 by NZVI for pH 9 and pH 2, the latter showed 99.2% removal of BY28 after a treatment time of 15 min, while the former had 26% removal efficiency. Therefore, the results of the BY28 degradation with different pH values confirm the importance of working in acid

medium.

3.4. Adsorption or degradation?

Under optimal conditions (i.e. NZVI dosage: 2G1-1; contact time: 15 min and pH: 2), the BY28 removal efficiency of 98.2% was obtained. The BY28 removal steps are shown in Figure 6.

To demonstrate the formation of degradation products during treatment, the degradation products were followed using HPLC. A BY28 solution (100 mg L⁻¹) was treated by the Fe⁰ (2g L⁻¹) within 15 min under acidic conditions. Figure 7 shows chromatograms of the initial solution and after treatment of the BY28 dye by NZVI. After 15 min the BY28 peak appearing at retention time 11.5 min was no more observed.

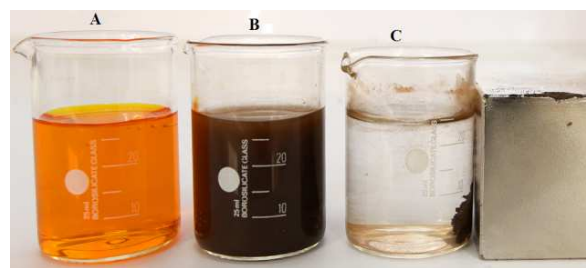


Figure 6: Images of the BY28 removal steps: (a) BY28 solution before addition of the NZVI, (b) BY28 solution after addition of NZVI and (c) BY28 solution after being exposed to a very strong magnet.

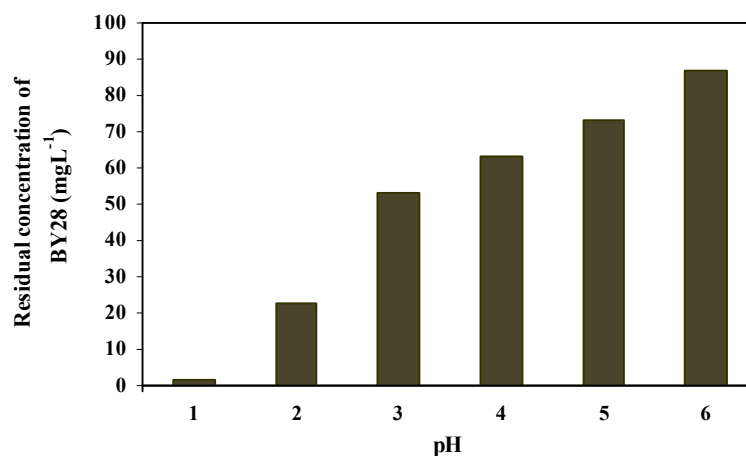


Figure 5: Effect of initial pH on the removal of BY28 by NZVI.

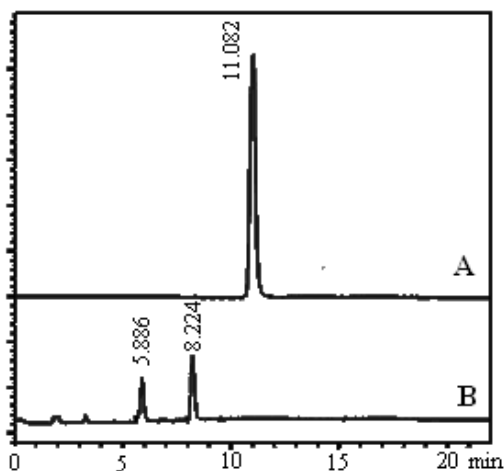


Figure 7: Comparison of HPLC profiles of (A): untreated (control) and (B): Fe^0 treated BY28 (NZVI dosage: 2gL^{-1} , BY28 concentration: 100 mg L^{-1} , pH: 2 and time of reaction was 15 min).

As it can be appreciated in Figure 7, there are two new chromatographic peaks (degradation products) after 15 min, which presented smaller retention times than the BY28 molecule. This indicates the presence of

compounds exhibiting less hydrophobicity (regarding the reverse stationary phase) and correspondingly lower carbon atom number than the original dye molecule.

In addition, to discriminate the adsorption or degradation of the BY28 with NZVI, the BY28-treated NZVI was extracted thoroughly in water and methanol, and the extract did not present the absorption band of the BY28; proves that BY28 removal was not through adsorption.

4. Conclusions

To the best of our knowledge, this is the first report on the treatment of a solution containing cationic and azomethine dye using zero-valent iron. The degradation of an azomethine dye (BY28) by zero-valent iron powder in aqueous solution was studied. The results showed that the degradation is influenced by solution acidity and NZVI dosage, and with decreasing the acidity and increasing the NZVI dosage, the degradation efficiency increases. The synthesized ZVI particles of nanoscale size exhibited effective decolorization for BY28 dye and under optimal conditions (NZVI dosage of 2gL^{-1} ; contact time of 15 min and pH 2), more than 98% of the dye is removed.

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