

RAPID DEGRADATION OF AZO DYES USING NANO-SCALE ZERO VALENT IRON

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ABSTRACT

In the present study, nano-scale Zero Valent Iron (NZVI) was synthesized in ethanol medium by the method of ferric iron reduction using sodium borohydride as a reducing agent under atmospheric conditions. The obtained iron nanoparticles are mainly in zero valent oxidation state and remain without significant oxidation for hours. A systematic characterization of NZVI was performed using XRD, SEM and TEM studies. The obtained iron nanoparticles consist of a zero valent core surrounding a rest oxide shell. The diameter of iron nanoparticles was predominantly within the range 20-110 nm. Refractory azo-dye compounds used in the textile industry are commonly detected in many industrial waste water. In this study the removal efficiency of three azo dyes, namely, methyl orange, sunset yellow and acid blue a, with laboratory synthesized NZVI particles in relation to the NZVI dosage, dye concentration and pH was determined. Increasing the dose of NZVI particles enhanced the decolonization of the dyes. The degradation decreased with increasing solution pH and concentration of dyes. These findings demonstrated the fast removal of azo dye compounds with NZVI and the advantage of the synthesized NZVI particles to treat azo dye contaminated wastewater.

Keywords: Nano-Scale Zero Valent Iron, Removal Efficiency, Decolonization, Degradation, Azo Dyes

1. INTRODUCTION

Azo dyes comprise of almost half of global production (700, 000 t/y) and during dyeing operation processes about 20 % of them end up in wastewaters (Azbar *et al.*, 2004). Aromatic azo-dyes comprise about half of the total international dye market (Wang and Zhang, 1997; Kulkarni *et al.*, 1985). Textile wastewaters contribute to a significant amount of pollution all over the world, mainly because of the presence of brightly colored dyes and their recalcitrant nature to degradation. This is because of the presence of the chromophore N = N, called the azo bond, which gives it its color (VUS, 2013).

Since the first dye was discovered in 1856 to present time, over thousands of different types of dyes have been invented (Dhuinshleibhe, 2013; EB, 2013; Susan, 2013). As a result, over hundreds and thousands of tons of dyes were manufactured. As the number of dye production increased so did the amount that was being disposed. The

sources of effluent with dyes come from industries mainly, such as, dyeing and printing, textiles, paper and ink manufacturing industries, cosmetics, pharmaceuticals, food (Wallace, 2001; Chequer *et al.*, 2011).

Dye is very harmful to both the environment and the living organisms. Unfortunately, in countries like Bangladesh, these sort of effluents are directly disposed off into water bodies with minimal or no treatment. The resulting effects of this are that, a color is imparted on the water body (Chequer *et al.*, 2011). This increases the turbidity and thus reduces the penetration of light into water. The aquatic plants are the biggest sufferers as they are not able to carry out photosynthesis. It also endangers other aquatic lifeforms which eventually leads to a disturbance of the aquatic ecosystem (Chequer *et al.*, 2011).

They can also cause skin cancer thus posing as an occupational hazard for people working in the cosmetic and other dye related industries. In addition, it can form biotransformation products when interacting with other elements in the environment which in turn pose

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different threats and risks to humans, animals and the environment (Chequer *et al.*, 2011). Thus, it has become imperative to treat the dyes before their discharge into the environment.

There are many treatment methods out there but most of them if not all have shortcomings. The azo dyes are highly resistant to micro-organisms making the biological treatment on them ineffective. Also, degradation by physical-chemical treatments such as activated carbon sorption, UV light-degradation, ozonation, nanofiltration and chemical oxidation-reduction treatments are equally if not less inefficient (Perey *et al.*, 2002).

Recently, people have been studying and developing the uses of nanotechnology (Shan *et al.*, 2008; Celebi *et al.*, 2007). Nano-scale Zero Valent Iron (NZVI) particles represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems (Shan *et al.*, 2008). Research has shown that nano-scale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides and Polychlorinated Biphenyls (PCBs) (Shan *et al.*, 2008).

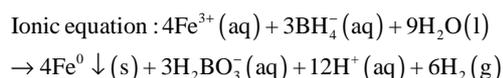
NZVI is extremely small with its diameter ranging from 50 to 100 nm, which gives it a large surface area: Volume ratio and makes it highly reactive by its high surface reactivity (Ponder *et al.*, 2000). Thus, it has a greater chance of coming into contact with dye molecules and hence decolorizing them.

Furthermore, their surface areas are up to several times greater than larger-sized powders or granular iron (Ponder *et al.*, 2000; Yuvakkumar *et al.*, 2011). This characteristic makes NZVI particles much more reactive in a reduction-oxidation (redox) process. Because of its extremely small size and high surface area, NZVI is thought to be a more effective technology for dye effluent treatment. An enlarged surface area allows the NZVI particles to react at a much higher rate with azo dyes. This potentially improves degradation performance in high concentration portions of the dyes. Small particle size also allows much more mobility into the dye effluent and NZVI can more easily be injected into shallow and deep dye effluent stores than granular iron (Schmid *et al.*, 2013). Equally important, they provide enormous flexibility for *in situ* applications (Schmid *et al.*, 2013; EE, 2013). Ability to inject iron can be advantageous when contamination underlies a building.

2. MATERIALS AND METHODS

2.1. Preparation of NZVI

For the synthesis of the NZVI particles, 1.0812 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in a 4/1 (V/V) ethanol/water mixture (48 mL ethanol and 12 mL deionized water) and stirred well. On the other hand, 0.7566 g of NaBH_4 was dissolved in 200 mL of deionized water to make a 0.1 M solution. An excess was prepared to ensure complete reduction into NZVI particles. As the NaBH_4 solution was added to FeCl_3 solution, black particles immediately formed. The solutions were mixed completely and then were vacuum filtered to separate the NZVI particles. After that, these were rinsed three times with ethanol to remove all the water. This is a key step as it helps prevent the rapid oxidation of the particles. Then they were stored in a bottle covered with ethanol and placed in a desiccator till further use. Following is the ionic equation for the reduction of ferric iron to NZVI:



2.2. Preparation of Dye Solution

100 ppm solutions of each of the three azo dyes were prepared by dissolving 25 mg in 250 mL of distilled water. They were placed inside a vacuum oven for 1 hour at 100°C to absorb any moisture present. Further concentrations of 5, 25, 50 and 75 ppm solutions of each dye were prepared.

2.3. Decolonization of Dyes

Pre-weighted amount of NZVI were added to the different dye samples. Absorbance readings of the dye samples were measured using a spectrophotometer (Model- DR/4000U Hach Company, USA) before and after the addition of NZVI.

Different parameters such as pH, concentration of dye and NZVI were varied to study their effects on the degradation process.

4. RESULTS

4.1. Characterization of NZVI Particles

The NZVI particles when preserved with a layer of ethanol stayed without significant oxidation for several weeks. A systematic characterization of the particles were performed using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD). The images are given below in **Fig. 1 and 2**.

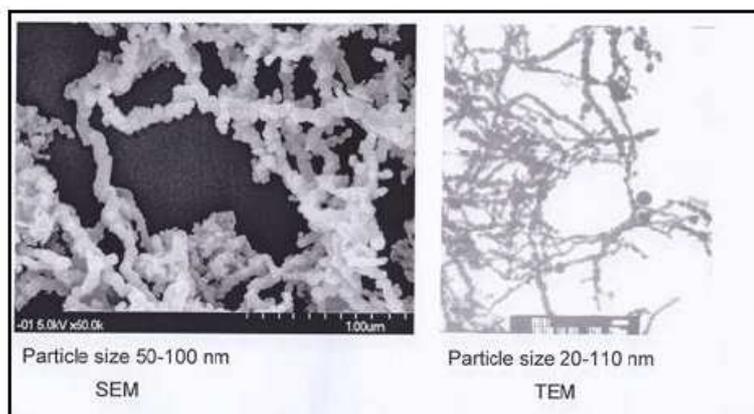


Fig. 1. SEM and TEM images of NZVI

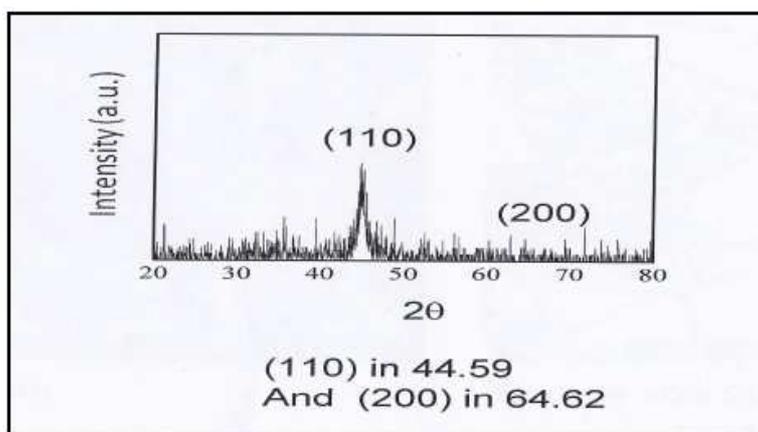


Fig. 2. XRD image of NZVI

Figure 2 shows the SEM image of freshly prepared NZVI particles. The SEM image and TEM image are in agreement of the nano particle diameter.

They represent nano-spherical iron particles that form chain like aggregations due to its magnetic properties. In addition, the images show that these particles have diameters between 20 to 110 nm, which indicates good quality iron particles. Furthermore, this leads on to prove that NZVI has a large surface area: Volume ratio. Due to this property, it is highly reactive and therefore can participate more in re-actions bringing about the breakdown of the dye particles in the solution.

From the XRD image in **Fig. 2**, it can be deduced that the wide peak is due to the presence of an amorphous state of iron. Also, the broad peak at 2θ of 45° is characteristic of NZVI and proves the existence of a great amount in the sample (Yuvakkumar *et al.*, 2011).

4.2. Effect of NZVI Dosage on Different Concentrations of Dye Solutions

0.5 g of NZVI was added to 5 mL of 5, 25, 50, 75 and 100 ppm of all the three dye solutions. This was studied to see how the degradation is affected with increasing concentrations of dye molecules while keeping a constant amount of NZVI. A control was set up by keeping equal concentrations (5 mL of 5, 25, 50, 75 and 100 ppm of all the three dye solutions) of the dye samples in the same conditions without any addition of NZVI.

As can be seen from **Fig. 3**, the absorbance is significantly less after addition of NZVI. The graphs of **Fig. 3** show a clear increasing trend of absorbance with the increase in concentration of dye as NZVI was added. All in all, it can be deduced that the absorbance after treatment with NZVI in all the cases is significantly less than that before treatment.

However, the trend of amount of decolorization for each case may vary a little, but overall, it can be concluded, as observed from methyl orange that as the concentration of the dye increased so did the absorbance after treatment. This was because the amount of NZVI was kept constant, so as the amount of dye increased, there were more particles of the latter that the former could not breakdown due to being outnumbered.

Furthermore, the percentage of dye removed was calculated by the equation given below. In this case, the absorbance taken is that of the mother solutions to which 2 g of NZVI had been added:

$$\% \text{ Decolorized} = \frac{\text{Initial Absorbance} - \text{Final Absorbance}}{\text{Initial Absorbance}} \times 100 \%$$

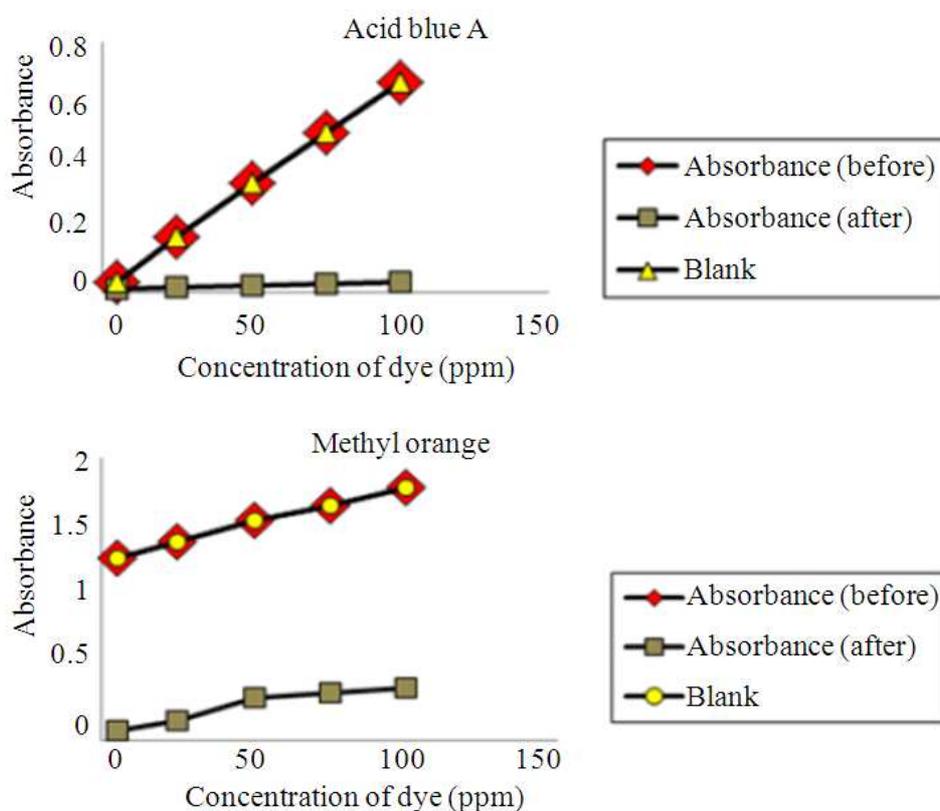
The results are given in **Table 1**. It is evident that the percentage removal of the dyes by NZVI was well over 90 % for the first two dyes and almost 80 % for methyl orange. A significant amount as can be seen has been degraded by NZVI.

Table 1. Percentage removal of dyes with NZVI

Initial absorbance	Final absorbance	Percentage removed
Sunset yellow = 1.506	Sunset yellow = 0.017	Sunset yellow = 98.9%
Acid blue A = 0.773	Acid blue A = 0.009	Acid blue A = 98.8%
Methyl orange = 1.884	Methyl orange = 0.378	Methyl orange = 79.9%

4.3. Effect of Varying NZVI Dosages on Dye Samples

This section attempts to find out the dosage required to achieve a significant reduction of concentration of dye samples. Varying dosages of 0.25, 0.5, 1, 1.5 and 2 g of NZVI were added to 10 mL of all the 100 ppm dye solutions. Further analysis of which will be followed by the graphs given below in **Fig. 4**. A control was set up by keeping equal concentrations (10 mL of 100 ppm dye solutions) of the dye samples in the same conditions without any addition of NZVI.



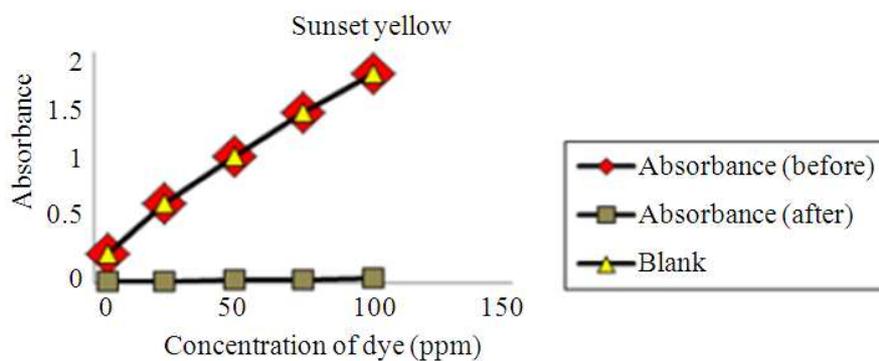


Fig. 3. Effect of various dye concentrations on decolonization

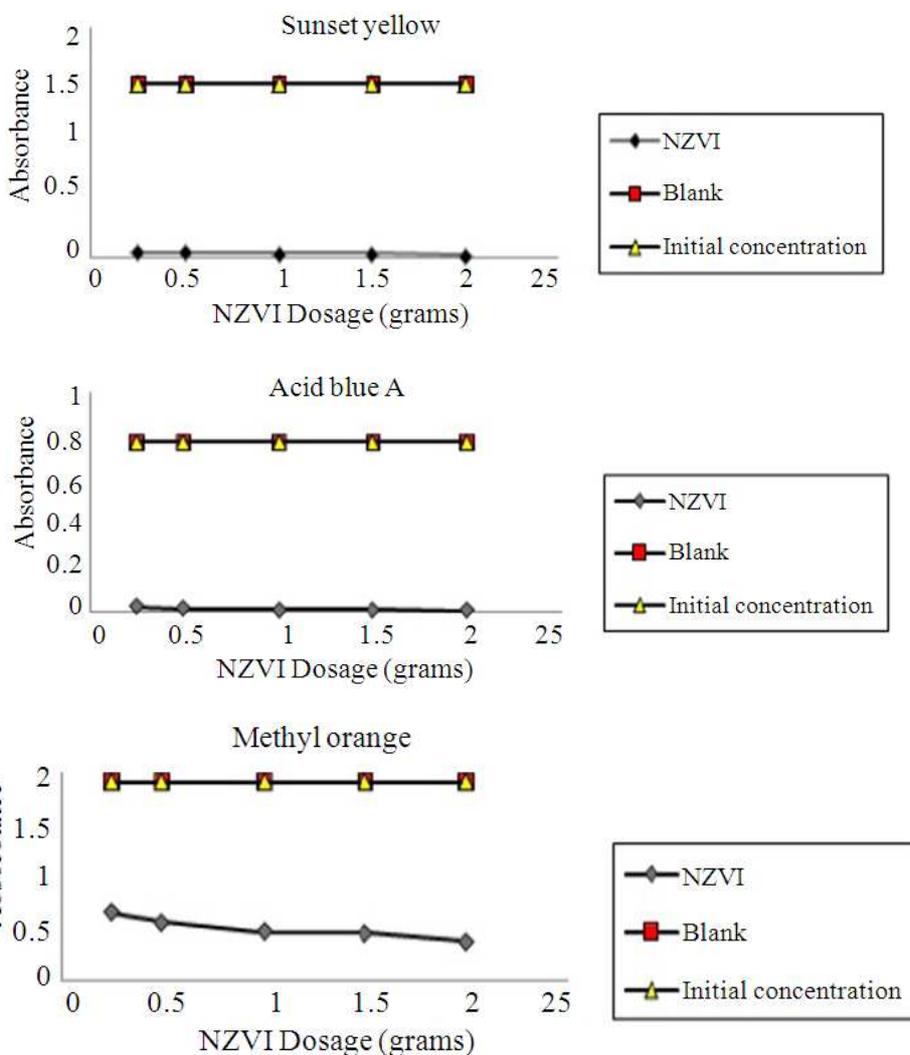


Fig. 4. Effect of various NZVI dosages on decolonization

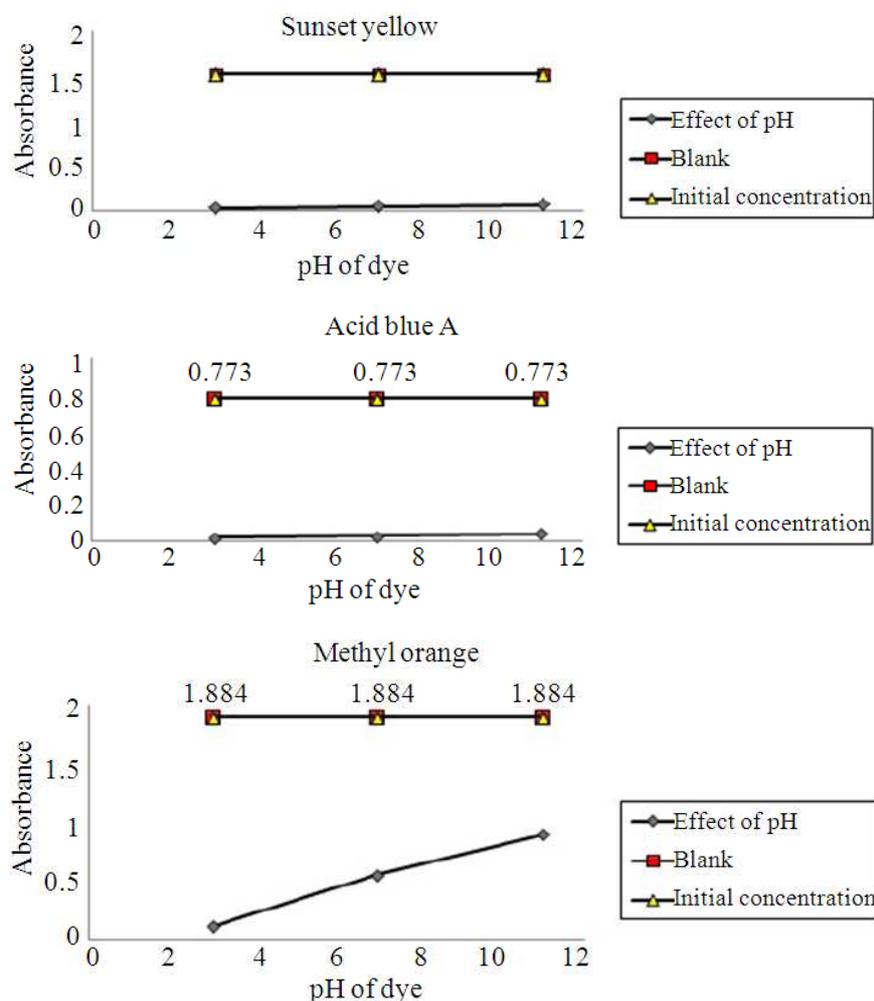


Fig. 5. Effect of pH on dye Decolorization

All the graphs in **Fig. 4** prove that with the increasing dosage of NZVI, the decolorization was greater. As there were more particles in the solution to take part in the reaction, with an increased surface area, there were more surface sites available to break down more dye particles and render them colorless.

4.4. Effect of pH on Dye Samples Treated with NZVI

This section expresses the amount of degradation with changes in pH level. 0.5 g of NZVI was added to 10 mL of all the 100 ppm dye solutions. The pH of these solutions was adjusted to 3, 7 and 11. A control was set up by keeping equal concentration (10 mL of 100 ppm dye solutions) of the dye samples with

varying pH levels (3, 7 and 11) in the same conditions without any addition of NZVI.

All in all, from **Fig. 5** it is evident that degradation increases with a decrease in pH. With lower pH, there are a greater number of hydrogen ions present. The iron particles donate two electrons to the H^+ ions converting them into atoms. These atoms in turn attack the dye particles, breaking them down to amines and rendering them colorless. As the solution gets more acidic, there are a great amount of H^+ ions present, thus, iron particles can donate electrons to more ions turning them to atoms (Chatterjee *et al.*, 2010). These in turn can attack the azo bonds more at an increasingly acidic condition bringing about disruptions in more dye molecules. This is depicted by the graphs below in **Fig. 5** which show a greater degradation with a decreasing pH.

5. CONCLUSION

From the experiments performed in this study, it can be said that NZVI is an effective degrading agent for dyes. It works best in acidic conditions when the amount of H⁺ ions is greater. Fe²⁺ ions are formed after the reduction by NZVI and are quite simple to remove by precipitation.

The removal efficiency is also high with more or less all the dyes being well over 90%.

In countries like Bangladesh, where the disposal of untreated waste water is a serious issue, NZVI could be a promising solution for this problem. It is cheap and readily available. Also, there is hardly any hassle in its preparation. Moreover, the end product is colorless and therefore can be discharged into nearby water bodies without any adverse consequences to turbidity and similar conditions.

6. ACKNOWLEDGEMENT

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