



Degradation of Azo Dyes Wastewater by Nanoscale Zero Valent Iron

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ABSTRACT

Wastewater from fabric and yarn dyeing impose serious environmental problems because of their colour and potential toxicity. The release of coloured wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication, and perturbations in aquatic life. Decolorization of their high colour and organic concentration is serious. In this decade, innovation methods have been developed such that nanoscale zero valent iron particles applied in environmental treatment have emerged dynamically and promptly. In this study, it was attempted to decolourize azo dye wastewater using the nanoscale zero valent iron particles. The effects of pH in solution, the zero valent iron dosage, reaction time and the initial dye concentration on the degradation rate were investigated. The results showed that those factors played an important role on the degradation of the dye by the nanoscale zero valent iron.

INTRODUCTION

Wastewater from fabric and yarn dyeing impose serious environmental problems because of their colour and potential toxicity. The release of coloured wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication, and perturbations in aquatic life (He et al. 2012). Decolorization of their high colour and organic concentration is serious. The most groups of commercial dyes used in the textile industries are azo dyes. Azo pigments have the common structure (-N=N-), which is conjunct to carbon atoms in the both sides with sp^2 hybrid (Marcio et al. 2017). Azo groups are usually conjunct to convoluted aromatic systems and the stability of aromatic structures is dangerous for environment (Suvanka et al. 2016). Thus, the dye wastewater must be treated before discharge as to minimize the threat to the environment. However, removal of colour from dye wastewater is a great challenge. At present, the major techniques for treating dye wastewater are adsorption process and biological treatment (Chen et al. 2011). Activated carbon, due to its porous property with large specific surface area, can be an ideal adsorbent for dye wastewater. Biological treatment that involves microbial activities can be energy saving and low cost. Nonetheless, there are disadvantages associated with each of these techniques (Mahmoud et al. 2014). For example, activated carbon adsorption only transfers the dye wastewater from the liquid phase to the solid phase. The biological process is difficult to start up and control. Furthermore, the organics in the

wastewater cannot be degraded completely by biological processes and as a result the total treatment cost can increase because of the need of further treatment (Lin et al. 2008).

In this decade, innovation methods have been developed such that nanoscale zero valent iron particles applied in environmental treatment have emerged dynamically and promptly (Djurdja et al. 2014). The nanoscale zero-valent iron particles with large surface area per unit mass have been found to be highly efficient reducing agent capable of remediating contaminated land, surface and groundwater. The advantages of the technology are low cost, low toxicity, small footprint and easy to get, which can satisfy the basic requirements for industrial application (Wang et al. 2016). The nanoscale zero-valent iron has been reported to be a strong reducing agent for rapidly reducing the chlorinated organic compounds, hexavalent chromium and nitrate. Also, an increasing number of field tests including pilot scale and full scale remediation sites have been occupied by using the nanoscale zero valent iron (Wang et al. 2015, Lin et al. 2008).

The nanoscale zero valent iron has been reported to decolourize azo dye solution through the reduction of the azo bond through surface mediated reaction. The cleavage of the azo bond in the chromophore of an azo dye leads to decolorization of the dye solution (Wei et al. 2013).

In this study, it was an attempt to decolourize azo dye wastewater using the nanoscale zero valent iron particles.

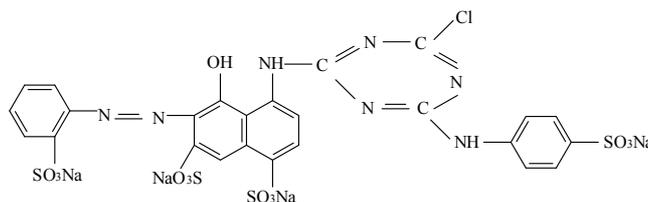


Fig. 1: The chemical structure of the C.I. Reactive Red 15.

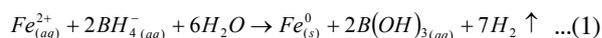
The data of the experiment on the decolorization of azo dye wastewater was reported to understand the mechanism of azo dye reduction by the nanoscale zero valent iron particles. The effects of the initial pH value, the reaction time, the nanoscale zero valent iron dosage and the initial dye concentration on azo dye decolorization were investigated.

MATERIALS AND METHODS

Dyes and chemicals: The dye of C.I. Reactive Red 15 was chosen as an object in this experiment. It was purchased from Shanghai Chemical Co. Ltd. in China. Its molecular formula is $C_{25}H_{14}ClN_7Na_4O_{13}S_4$. Its chemical structure is shown in Fig.1.

Following chemicals were also used in the experiments, such as KBH_4 , $FeCl_2 \cdot 4H_2O$, $(CH_3)_2CO$ and polyvinylpyrrolidone K-30. All the reagents were of analytical grade. They were purchased from Shanghai Chemical Co. Ltd. in China and used without any further purification.

Preparation of the nanoscale zero valent iron: The nanoscale zero valent iron was synthesized in the laboratory using a method modified from previous liquid phase method by adding the macromolecule stabilizer. The basic principle of the synthesis process was that, ferrous ion was rapidly reduced to the nanoscale zero valent iron by borohydride solution following the equation below:



The concentration of 100 mL 0.02 M ferrous chloride solution was prepared and then 4 g PVP was added into the ferrous chloride solution in a beaker with vigorous stirring that PVP was completely dissolved. The 100 mL 0.06 M potassium borohydride solution was swiftly added into the above solution and the mixture was agitated in a water bath shaker with a shaking rate of 120 rpm at 15°C until the solution turned into black without rising bubbles. The nanoscale zero valent iron was washed with propanone three times in order to clean up the residual reagent, and then they were soaked with propanone in the beaker ready for test.

Experimental procedure: Bath experiments were conducted by mixing 250 mL of dye solution and the nanoscale zero valent iron particles in 250 mL Erlenmeyer flasks. The

flasks were shaken at 150 rpm and a pH probe for the determination. All the decolorization tests were performed twice, and the average values were used.

Analytical methods: The value of pH was measured with a pH probe according to APHA Standard Method. The concentration of dye C.I. Reactive Red 15 was measured with a UV-1600 spectrophotometer at 510 nm.

The removal rate of dye C.I. Reactive Red 15 was calculated as following:

$$Q = \frac{C_0 - C_t}{C_0} \times 100\% \quad \dots(2)$$

Where, C_0 and C_t (mg/L) are the initial and equilibrium concentrations of dye C.I. Reactive Red 15 in solution respectively. Q is the degradation rate of dye C.I. Reactive Red 15.

Statistical analyses of data: All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All error estimates given in the text and error bars in figures are standard deviation of means (mean \pm SD). All statistical significance was noted at $\alpha=0.05$ unless otherwise stated.

RESULTS AND DISCUSSION

Physical properties of the nanoscale zero valent iron: The structures and sizes of the nanoscale zero valent iron were characterized and identified by scanning electron microscopy, as shown in Fig. 2.

This image shows the SEM image of freshly synthesized iron nanoparticles. The synthesized zero valent iron particles were basically spherical shaped and scattered evenly. It can be demonstrated that the zero valent iron particles are in the form of nanosphere, which exist in contact with each other and form chains having diameters of low 100 nm.

The effects of reaction time: In order to test the effects of reaction time, the reaction time is ranged from 1 min to 14 min. The experiments were tested by mixing 250 mg/L of dye concentration, pH 2.0 in solution and 2 g of the zero valent iron particles in 250 mL Erlenmeyer flasks. The ef-

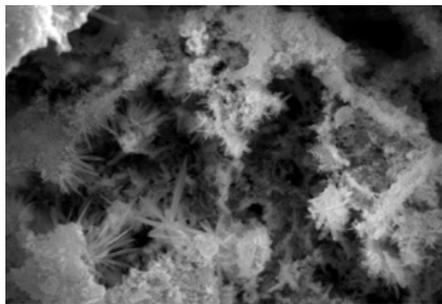


Fig. 2: The SEM image of the zero valent iron.

fects of reaction time on the degradation of dye C.I. Reactive Red 15 by zero valent iron are shown in Fig. 3.

From Fig. 3, it can be seen that the reaction time had an important role on the degradation rate. Apparently, the degradation speed was very fast. The degradation process finished in 6 min. Therefore, the 2 min of the reaction time was chosen for the following experiments.

The effects of the initial pH value: The value of pH in solution is an important parameter affecting azo dye removal. The actual dye containing wastewater has a wide range of pH values, so it is very necessary to investigate the influence of pH in solution on decolorization process. The initial pH value was ranged from 2.0 to 11.0. The experiments were tested by mixing 250 mg/L of dye concentration and 2 g of the zero valent iron particles in 250 mL Erlenmeyer flasks. The reaction time was 2 min.

The effects of initial pH value on the degradation of dye C.I. Reactive Red 15 by zero valent iron are shown in Fig. 4. From Fig. 4, it can be seen that the value of pH in solution had an important effect on the degradation rate of dye C.I. Reactive Red 15. The degradation rate of the dye decreased with increasing the value of pH in solution. The results indicated that the value of pH in solution played an important role in the degradation of dye C.I. Reactive Red 15 by zero valent iron. Apparently, the degradation processes were acid driven for dye C.I. Reactive Red 15. The possible reason might be that the zero valent iron which carried positive charges at low pH value repulsed the approach of the positively charged dye molecule, leading to relatively low degradation rate. While at high pH value, electrostatic repulsion was decreasing (Nathalie et al. 2017).

The effects of the zero valent iron dosage: In order to test the effects of the zero valent iron dosage, the zero valent iron dosage is 1, 2, 3, 4 and 5 g respectively. The experiments were tested by mixing 250 mg/L of dye concentration and pH 2.0 in solution in 250 mL Erlenmeyer flasks. The reaction time was 2 min. The effect of the zero valent iron dosage on the degradation of dye C.I. Reactive Red 15

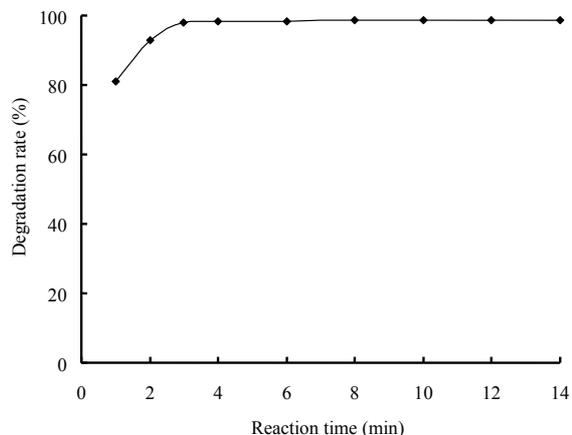


Fig. 3: Effect of reaction time on the degradation rate.

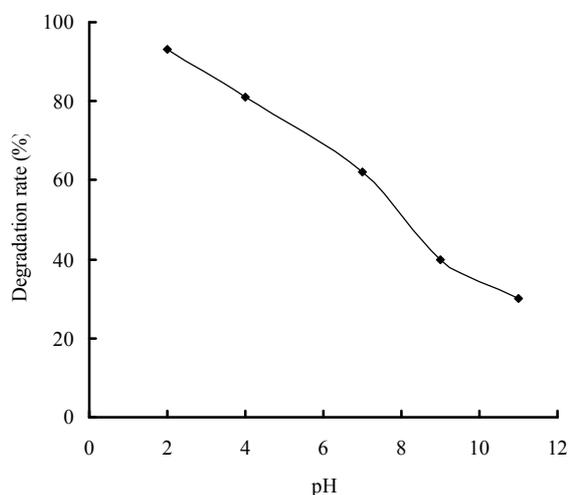


Fig. 4: Effect of initial pH in solution on the degradation rate.

is demonstrated in Fig. 5.

From Fig. 5, it can be seen that the degradation rate of dye C.I. Reactive Red 15 increased with increasing zero valent iron dosage. The increased total surface area and availability of more zero valent iron sites may be the reason for the rise in degradation efficiency with increasing the zero valent iron dosage (Invana et al. 2012).

The effects of the initial dye concentration: The initial dye concentration is an important factor for the degradation rate of dye. The experiments were tested by 2 g of the zero valent iron particles and pH 2.0 in solution in 250 mL Erlenmeyer flasks. The reaction time was 2 min. The experimental results are shown in Fig. 6.

As shown in Fig. 6, it can be concluded that the initial dye concentration had an important effect on the degradation rate. As the initial dye concentration increased, the degradation rate of the dye decreased.

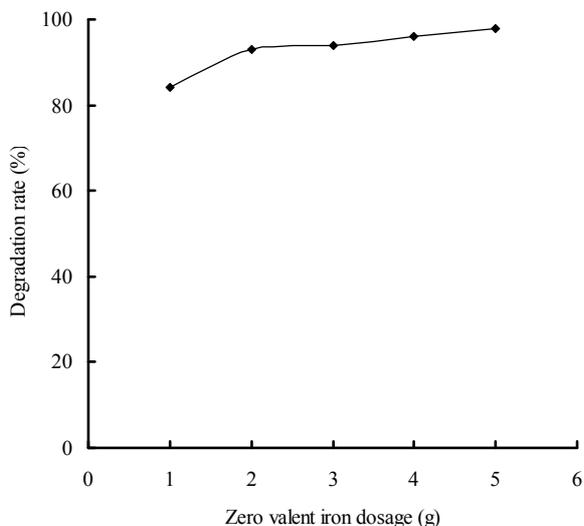


Fig. 5: Effect of zero valent iron dosage on the degradation rate.

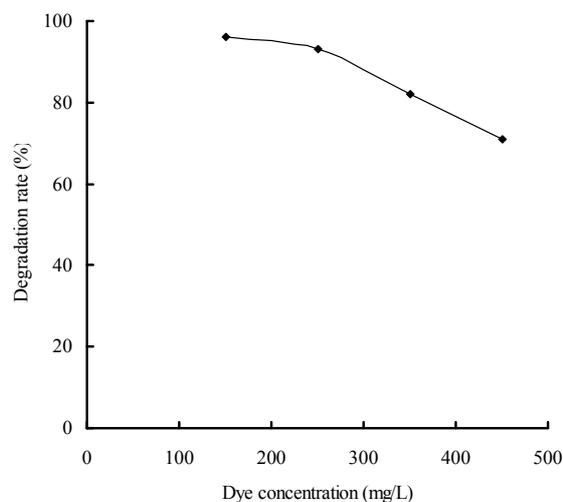


Fig. 6: Effect of the initial dye concentration on the degradation rate.

CONCLUSIONS

The synthesized zero valent iron particles were basically spherical shaped and scattered evenly. It can be demonstrated that the zero valent iron particles are in the form of nanosphere, which exist in contact with each other and form chains having diameters of low 100 nm. Then, it was an attempt to decolourize azo dye wastewater using the nanoscale zero valent iron particles. The effects of pH in solution, the zero valent iron dosage, reaction time and the initial dye concentration on the degradation rate were investigated. The experimental results showed that the degradation rate of dye was high. The influencing factors, such as contact time, pH in solution, the zero valent iron dosage and initial concentration of dye, had an important influence on the degradation rate.

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