Nature Environment and Pollution Technology *An International Quarterly Scientific Journal*	p-ISSN: 0972-6268 e-ISSN: 2395-3454	Vol. 17	No. 2	pp. 479-483	2018

Original Research Paper **Open Access**

Study on the Degradation of Azo Dye Wastewater by Zero-valent Iron

Guijia Qiu*, Yuanyuan Wu, Luyi Qi*, Chengguang Chen*, Linfa Bao*** and Muqing Qiu***†**
*College of Pharmacy and Health, Shaoxing University Yuanpei College, Shaoxing, 312000, P.R. China
**Department of Environmental Monitor Station, Qingtian, Zhejiang, 323900, P.R. China
***College of Life Science, Shaoxing University , Shaoxing, 312000, P.R. China
†Corresponding author: Muqing Qiu

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 19-06-2017
Accepted: 21-08-2017

Key Words:
Decolorization
Azo dye wastewater
Zero-valent iron
C.I. reactive red 15

ABSTRACT

Wastewater from fabric and yarn dyeing impose serious environmental problems because of their colour and potential toxicity. The release of coloured wastewaters in ecosystems is a dramatic source of aesthetic pollution, eutrophication and perturbations in aquatic life. The most common group of commercial dyes used in the textile industries is azo dyes. The degradation of azo dye wastewater by zero-valent iron was investigated. The dye of C.I. Reactive Red 15 was chosen as object in the experiment. The effects of the dosage of zero-valent iron, pH in solution, reaction time and the initial azo dye concentration on the decolorization were studied in detail. The results showed that the pH value, the dosage of zero-valent iron and the initial azo dye concentration had an important impact on azo dye decolorization. High decolorization efficiency of azo dye wastewater by zero-valent iron was achieved under the optimal condition. The zero-valent iron was also proved to be a universal and efficient reductant for rapid decolorization of the azo dye wastewater. This method can be applied into the treatment of the azo dye wastewater.

INTRODUCTION

Dyes are widely used in the textile and dyestuff industries. The textile industry is one of the largest producers of effluents contaminated with dyes (Peng et al. 2017). Thus, a number of coloured effluents that contain dyes are released from this industry. The residual dyes released from these effluents introduce different organic pollutants in the natural water resources and land (Alkan et al. 2008).

The wastewater from textile when directly released into the surface water without treatment can cause a rapid depletion of dissolved oxygen and lead to a great environmental damage. When dyes are available in the water system, the sunlight penetration into deeper layers is greatly reduced, which disturbs photosynthetic activity resulting in deterioration of water quality, lowering the gas solubility, and finally causing acute toxic effects on aquatic flora and fauna (Abbasi & Asl 2008). Most of the dyes that are released from wastewater, including their breakdown products, are toxic, carcinogenic, or mutagenic to humans and other life forms (Chidambaram et al. 2015). The most common group of commercial dyes used in the textile industries is azo dyes. They are usually conjunct to convoluted aromatic systems and the stability of aromatic structures is dangerous for environment. It is important to study the decolorization of azo dye wastewater (Kobya et al. 2014).

During the past years, many physicochemical methods for the removal of azo dyes wastewater have been reported, such as adsorption on activated carbon, electrocoagulation, flocculation, froth flotation, ion exchange, membrane filtration, ozonation, and reverse osmosis, are used for the decolorization of dyes in wastewater. These methods are inefficient, expensive, have less applicability, and produce wastes in the form of sludge, which again needs to be disposed off. On the other hand, biodegradation of dye is a challenge not only because of the low BOD/COD ratio, but also the presence of metals, metalloids, salts and other toxicants (Imran et al. 2015). Conventional and innovative biological processes have been tried, including adsorbent assisted biodegradation using sequencing batch reactor (Santos & Boaventura 2015), aerobic-anaerobic bacteria (Popli & Patel 2015), and packed bed reactor using a consortium of bacteria (Patel & Gupte 2015). While biological processes work to certain extent and they are difficult to be sustained in textile wastewater.

In recent years, the use of zero-valent iron, Fe^0 (ZVI) for the treatment of toxic chemicals in waters, has received wide attention. Zero-valent iron is a strong reducing agent, and it is cheap and easy to produce (Cundy et al. 2008). It has already been proven effective in reducing chlorinated solvents including chlorinated organics, nitroaromatic compounds, pesticides, nitrate, chlorinated organic compounds and metal ions (Lin et al. 2008, Epolito et al. 2008, Chang et al. 2009).

The degradation of azo dyes by zero-valent iron is of importance, not only for its potential utilization in the reduction of azo dye wastewater, but also because it could be

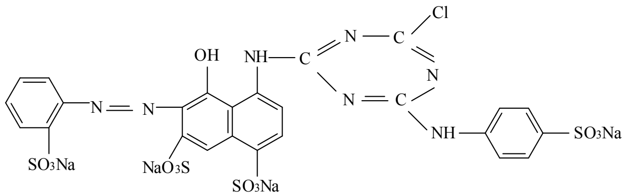

Fig. 1: The chemical structure of the C.I. Reactive Red 15.

applied as a pretreatment method prior to biological treatment. For azo dye wastewater treatment, a few researches demonstrate that high colour removal efficiency could be achieved by zero-valent iron in terms of its powerful reducibility. Thus, zero-valent iron can serve as a promising alternative technique to decolorize dye wastewater.

In this work, the degradation of azo dye wastewater of C.I. Reactive Red 15 by zero-valent iron was investigated. The effects of the dosage of zero-valent iron, pH in solution, reaction time and the initial azo dye concentration on the decolorization were studied in detail.

MATERIALS AND METHODS

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

The zero-valent iron was synthesized in the laboratory using the method modified from the previous liquid phase method by adding the macromolecule stabilizer, PVP (Vipulanandan et al. 2003). The basic principle of the synthesis process was that the ferrous ion was rapidly reduced to zero-valent iron by borohydride solution following the equation below (He et al. 2012):

$$Fe^{2+}_{(aq)} + 2BH^{-}_{4(aq)} + 6H_2O \rightarrow Fe^{0}_{s} + 2B(OH)_{3(aq)} + 7H_2 \uparrow \qquad ...(1)$$

All the chemicals in this study were of analytical grade and used without further purification.

Experimental methods: Degradation experiments were conducted in a set of 250 mL Erlenmeyer flasks containing zero-valent iron and 100 mL of dye C.I. Reactive Red 15 with initial concentrations in aqueous solution. The pH in solution was adjusted by (1+1) HCl and 10 % NaOH. The flasks were placed in a shaker at a constant temperature of 308 K and 120 rpm. The samples were then filtered and the residual concentration of dye C.I. Reactive Red 15 was analysed using a UV-1600 spectrophotometer at a wavelength corresponding to the maximum absorbance for dye C.I. Reactive Red 15.

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:

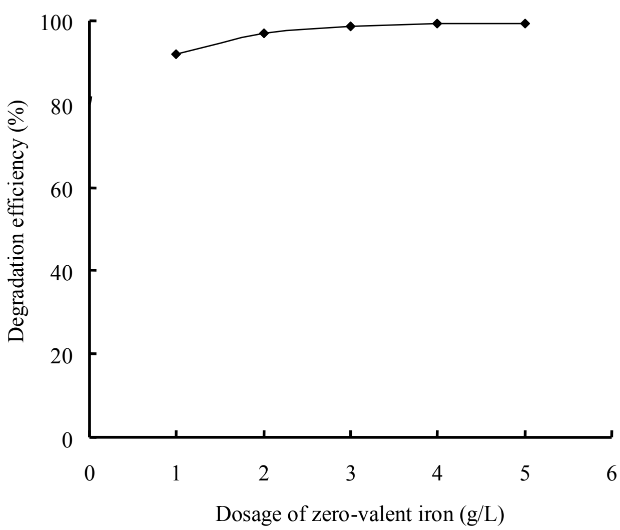

Fig. 2: The effect of the dosage of zero-valent iron on the degradation of dye C.I. Reactive Red 15.

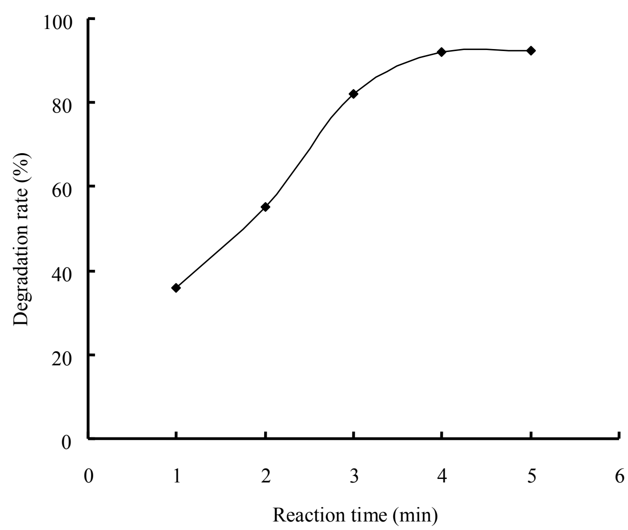

Fig. 3: The effect of the reaction time on the degradation of dye C.I. Reactive Red 15.

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

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 the 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±SD). All statistical significances were noted at α=0.05 unless otherwise noted.

RESULTS AND DISCUSSION

The effect of the dosage of zero-valent iron: The dosage of zero-valent iron is an important factor in the process. It is necessary to test the effect of the dosage of zero-valent iron. In order to investigate the role of zero-valent iron addition on the degradation of dye C.I. Reactive Red 15, a series of experiments were tested with different dosage of zero-valent iron from 1 g/L to 5 g/L. The other reaction parameters were temperature of 308 K, pH 2.0, 500 mg/L of dye C.I. Reactive Red 15 and reaction time of 5 min. The effect of the dosage of zero-valent iron on the degradation of dye C.I. Reactive Red 15 is shown in Fig.2.

From Fig.2, it can be seen that the degradation efficiency increased with increasing dosage of zero-valent iron. The increased total surface area and availability of more zero-valent iron sites may be the reason for the rise in degradation of dye C.I. Reactive Red 15 efficiency with increasing zero-valent iron dosage.

The effect of reaction time: The reaction time is one important factor affecting the degradation of dye C.I. Reactive Red 15. In order to investigate the effect of reaction time on the degradation rate, the following experiments were carried out. Degradation experiments were conducted in a set of 250 mL Erlenmeyer flasks containing zero-valent iron and 100 mL of dye C.I. Reactive Red 15 with initial concentrations in aqueous solution. The flasks were placed in a shaker at a constant temperature of 308 K and 120 rpm. The other reaction parameters were 1 g/L of zero-valent iron addition, 500 mg/L of dye C.I. Reactive Red 15 and pH 2.0. The samples were filtered and analysed at a various contact time ranged from 1 min to 6 min. The results are shown in Fig. 3.

From Fig. 3, it can be seen that the degradation rate was increased quickly at various contact times between 1 min and 3 min. However, when reaction time is ranged from 3 min to 5 min, the degradation rate increased slowly. After 6 min, the degradation process reached equilibrium slowly.

The effect of pH in solution: The pH value of the solution is an important parameter for the degradation of pollutants by zero-valent iron process. It can control the concentration of Fe^{2+} and the production rate of hydroxyl radical. So, it is very necessary to investigate the influence of pH in solution on decolorization process.

The effect of the initial pH value of the aqueous solu-

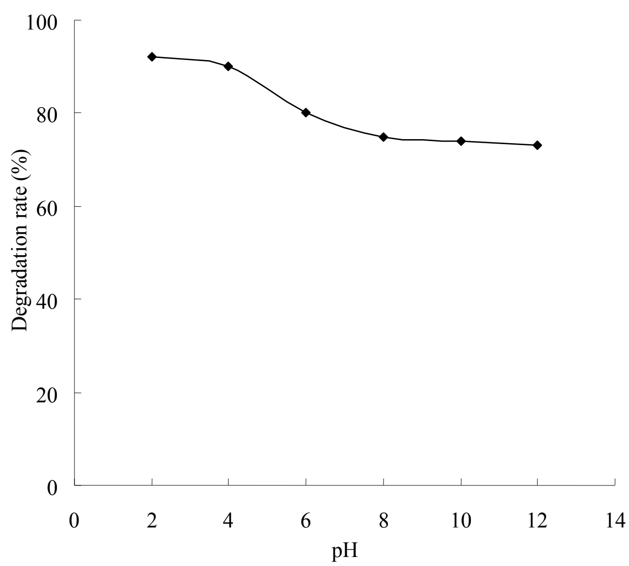

Fig. 4: The effect of pH in solution on the degradation of dye C.I. Reactive Red 15.

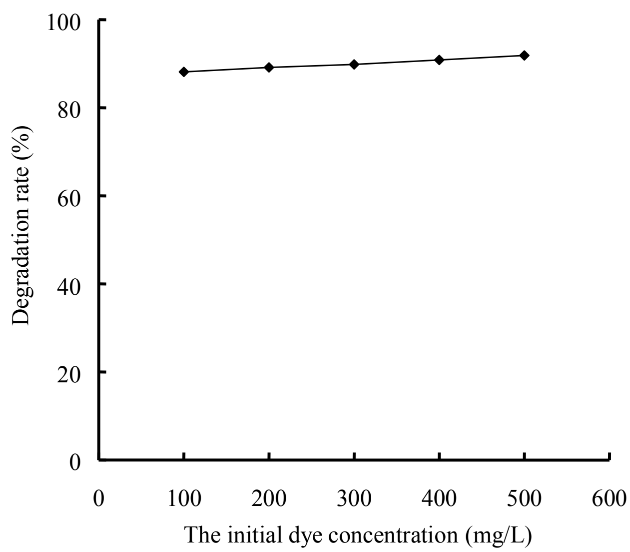

Fig. 5: The effect of the initial dye concentration on the degradation of dye C.I. Reactive Red 15.

tion on the removal rate of dye C.I. Reactive Red 15 was investigated at different pH in the range of 2.0 to 12.0. The other reaction parameters were temperature of 308 K, 1 g/L of zero-valent iron addition, 500 mg/L of dye C.I. Reactive Red 15 and reaction time of 5 min. The effect of pH in solution on the degradation rate of dye C.I. Reactive Red 15 is shown in Fig. 4.

Apparently, pH in solution has a strong effect on the degradation rate of dye C.I. Reactive Red 15. The degradation rate decreased as the pH in solution increased. So, the degradation process of dye C.I. Reactive Red 15 was in favour in acid solution. The main reason might be the strong reductive reaction and the oxidation of zero-valent iron (Vipulanandan et al. 2003). When the effective collision between dye molecular and zero-valent iron particles happened, the zero-valent iron as an electron donor was combined with H^+ and was turned into the transitional product (Mu et al. 2004). The iron corrosion in the presence of oxygen can generate hydrogen peroxide, because the reaction process was not protected by nitrogen gas. The hydrogen peroxide could react with the Fe^{2+} and produce strong oxidants such as hydroxyl radical and iron species. Thus, the mechanism of quick degradation of dye may be following reasons: The main reaction of strong reductive reaction was caused by zero-valent iron and side reaction of indirect oxidation was caused by hydroxyl radical and iron species (Zhang et al. 2005). Fe^{2+} ions as one of the reduction products could easily from ferrous hydroxide precipitates on the surface of zero-valent iron particles with pH increasing, covering the reactive sites and holding back the reaction process. This explained why degradation efficiency was low for dye C.I. Reactive Red 15 in alkaline condition (Sun et al. 2006).

The effect of the initial dye concentration: To investigate the effect of initial concentration of dye C.I. Reactive Red 15 on the degradation of dye from aqueous solution by the zero-valent iron, the experiments were carried out. The initial concentrations of dye C.I. Reactive Red 15 in aqueous solution were 50, 100, 200, 300, 400 and 500 mg/L respectively. The other operation conditions were temperature of 308 K, 1 g/L of zero-valent iron addition, pH 2.0 in solution and reaction time of 5 min. The experimental results are shown in Fig. 5.

As show from Fig. 5, it can be seen that the degradation rate of dye C.I. Reactive Red 15 varied with the initial dye concentration. The degradation rate decreased, when the initial dye concentration was increased.

CONCLUSIONS

In this paper, it was shown that the dosage of zero-valent iron, reaction time, pH in solution and initial dye concentration had an important effect on the degradation of dye C.I. Reactive Red 15 in aqueous solution. The degradation efficiency increased with increasing dosage of zero-valent iron. The degradation rate was increased quickly at various contact times between 1 min and 3 min. However, when reaction time is ranged from 3 min to 5 min, the degradation rate was increased slowly. The degradation rate decreased as the pH in solution increased. So, the degradation process of dye C.I. Reactive Red 15 was in favour in acid solution. The degradation rate decreased, when the initial dye concentration was increased. From the experimental results, the zero-valent iron was also proved to be universal and efficient reductant for rapid degradation of the azo dye wastewater.

ACKNOWLEDGEMENT

This study was financially supported by the project of the Science and Technology Plan in Shaoxing City (2015B70019 and 2017B70058) and the project of Shaoxing University Yuanpei College (Z20150015).

REFERENCES

Abbasi, M. and Asl, N.R. 2008. Sonochemical degradation of Basic Blue 41 dye assisted by nano TiO_2 and H_2O_2. J. Hazard. Mater., 153: 942-947.

Alkan, M., Dogan, M., Turhan, Y., Demirbas, O. and Turan, P. 2008. Adsorption kinetics and mechanism of maxilon blue 5G dye on sepiolite from aqueous solutions. Chem. Eng. J., 139: 213-223.

Chang, S.H., Wang, K.S., Chao, S.J., Peng, T.H. and Huang, L.C. 2009. Degradation of azo and anthraquinone dyes by a low-cost Fe-0/air process. J. Hazard. Mater., 166: 1127-1133.

Chidambaram, T., Oren, Y. and Noel, M. 2015. Fouling of nanofiltration membranes by dyes during brine recovery from textile dye bath wastewater. Chem. Eng. J., 262: 156-168.

Cundy, A.B., Hopkinson, L. and Whitby, R. 2008. Use of iron-based technologies in contaminated land and groundwater remediation: a review. Sci. Total Environ., 400: 42-51.

Epolito, W.J., Yang, H., Bottomley, L.A. and Pavlostathis, S.G. 2008. Kinetics of zero-valent iron reductive transformation of the anthraquinone dye Reactive Blue 4. J. Hazard. Mater., 160: 594-600.

He, Y., Gao, J.F., Feng, F.Q., Liu, C., Peng, Y.Z. and Wang, S.Y. 2012. The comparative study on the rapid decolorization of azo, anthraquinone and triphenylmethane dyes by zero-valent iron. Chem. Eng. J., 179: 8-18.

Imran, M., Crowley, D.E., Khalid, A., Hussain, S., Mumtaz, M.W. and Arshad, M. 2015. Microbial biotechnology for decolorization of textile wastewaters. Rev. Environ. Sci. Bio-technol., 14: 73-92.

Kobya, M., Gengec, E., Sensoy, M.T. and Demirbas, E. 2014. Treatment of textile dyeing wastewater by electrocoagulation using Fe and Al electrodes: optimization of operating parameters using central composite design. Coloration Technol., 130: 226-235.

Lin, Y.T., Weng, C.H. and Chen, F.Y. 2008. Effective removal of AB24 dye by nano/micro-size zero-valent iron. Sep. Puri. Technol., 64: 26-30.

Mu, Y., Yu, H.Q., Zhang, S.J. and Zheng, J.C. 2004. Kinetics of reductive degradation of Orange II in aqueous solution by zero-valent iron. J. Chem. Technol. Biotechnol., 79: 1429-1431.

Patel, Y. and Gupte, A. 2015. Biological treatment of textile dyes by agar-agar immobilized consortium in a packed bed reactor. Water Environ. Res., 87: 242-251.

Peng, X.X., Tian, Y., Liu, S.W. and Jia, X.S. 2017. Degradation of TBBA and BPA from aqueous solution using organo-montmorillonite supported nanoscale zero-valent iron. Chem. Eng. J., 309: 717-724.

Popli, S. and Patel, U.D. 2015. Destruction of azo dyes by anaerobic-aerobic sequential biological treatment: a review. Int. J. Environ. Sci. Technol., 12: 405-420.

Santos, S.C.R. and Boaventura, R.A.R. 2015. Treatment of a simulated textile wastewater in a sequencing batch reactor (SBR) with addition of a low-cost adsorbent. J. Hazard. Mater., 291: 74-82.

Sun, Y.P., Li, X.Q., Cao, J.S., Zhang, W.X. and Wang, H.P. 2006. Characterization of zero-valent iron nanoparticles. Adv. Colloid Interf., 120: 47-56.

Vipulanandan, F.L.C. and Mohanty, K.K. 2003. Microemulsion and solution approaches to nanoparticle iron production for degradation of trichloroethylene. Colloids Surf. A, 223: 103-112.

Zhang, H., Duan, L.J., Zhang, Y. and Wu, F. 2005. The use of ultrasound to enhance the decolorization of the C.I. Acid Orange 7 by zero-valent iron. Dyes Figments, 65: 39-43.