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Degradation of Azo Dye Acid Orange 7 by Zero Valent Iron Activated with Potassium Persulphate

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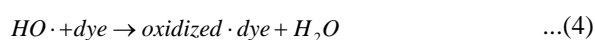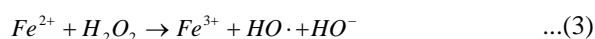
ABSTRACT

The zero valent iron has the advantage that the small particle size results in a large specific surface area and great intrinsic reactivity of surface sites. However, the zero valent iron particles tend to either react with surrounding media or agglomerate, resulting in significant loss of reactivity. The synthetic zero valent iron was activated by potassium persulphate. The degradation of azo dye Acid Orange 7 by zero valent iron activated with potassium persulphate was carried out. The effect of several parameters, such as the pH in solution, the reaction time, reaction temperature, the activated zero valent iron amount and the initial concentration of dye on the removal process was investigated. The results showed that the degradation rate of azo dye Acid Orange 7 by the activated zero valent iron was high. The operation parameters had an important effect on the degradation of azo dye Acid Orange 7 in aqueous solution.

INTRODUCTION

Dyes have been widely used in many industries, like textiles, printing, leather, paper, cosmetics and plastics. Discharge of sewage from those industries is an important threat to the environment (Cundy et al. 2008). The dye contaminated wastes can inhibit the sunlight from reaching the deep water, and resulting in the negative effect on growth of aquatic organisms (Sun et al. 2006). In particular, the accumulation of dyes in water environment is hazardous to the health of human health and other creatures because of its potential toxicity, carcinogenicity and teratogenicity (Djurdja et al. 2014). Azo pigments are applied into the industries widely. Azo groups are usually conjunct to convoluted aromatic systems and the stability of aromatic structures is dangerous for environment. Therefore, the degradation of dyes in solution is essentially necessary before they are discharged into the environment (Kanel et al. 2005).

Among the numerous dye removal techniques, adsorption is now the preferred method, which gives the best results in removing various types of colouring materials (Xiong et al. 2007). Nonetheless, there are some disadvantages associated with these techniques (Wang et al. 1998). For example, activated carbon adsorption only transfers the dyes from the liquid phase to solid phase. The biological process is difficult to start up and be controlled and also the organic compounds in the wastewater cannot be degraded completely by biological processes (Huang et al. 1998). Therefore, as a result, the total treatment cost can increase because of the need for further treatment. In the last decade, zero valent iron was used to destroy organic pollutants in water. This method has been proved to be a cost effective treatment approach and was widely used to treat wastewater containing chlorinated aliphatics, chlorinated aromatics and organic dyes (Devlin et al. 1998). A great deal of interest has developed in the degradation of dyes wastewater by zero valent iron particles, as they are inexpensive, environment friendly, easy to operate, and low iron concentration in effluent results in no further treatment demand (Gavaskar 1999). In most studies, the sole zero valent iron or supported zero valent iron was used for the effluent treatment (Linsebigler et al. 1995). The main mechanism of degradation of dye wastewater by zero valent iron was the reductive degradation of dye molecule (Eq. 1). The more recently zero valent iron particles are widely applied for wastewater treatment and organic compounds degradation in Fenton system (Papic et al. 2004). In acidic conditions, the surface of the zero valent iron particles corrodes and generates *in situ* ferrous ions, which leads to Fenton reactions in the presence of hydrogen peroxide (Eqs. 2-4). The zero valent iron particle surface can reduce the ferric ions down to ferrous ions, and then faster recycling of ferric iron at the iron surface occurs through Eq. 5 (Deng et al. 2000).

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad \text{...(1)}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad \text{...(2)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO \cdot + HO^- \quad \text{...(3)}$$

$$HO \cdot + dye \rightarrow oxidized \cdot dye + H_2O \quad \text{...(4)}$$

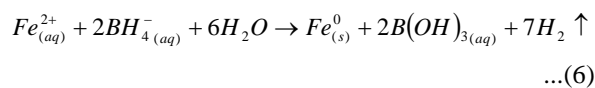$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \quad \text{...(5)}$$

The zero valent iron has the advantage that the small particle size results in a large specific surface area and great intrinsic reactivity of surface sites (Fu et al. 2014). However, the zero valent iron particles tend to either react with surrounding media or agglomerate, resulting in significant loss of reactivity (Sun et al. 2006). To prevent particle aggregation, a wide variety of stabilizers have been proposed to modify the zero valent iron particle surface characteristics (Shu et al. 2009).

In this study, the dye Acid Orange 7 was chosen in the experiment, because it is an extensively used dye in the textile industry. The synthetic zero valent iron was activated by potassium persulphate. The degradation of azo dye Acid Orange 7 by potassium persulphate activated using zero valent iron was carried out. The effect of several parameters, such as the pH in solution, reaction temperature, the reaction time, the activated zero valent iron amount and the initial concentration of dye on the removal process was discussed in detail.

MATERIALS AND METHODS

Dyes and chemicals: The dye Acid Orange 7 was chosen as an object in this experiment to be removed from water. It was purchased from Shanghai Chemical Co. Ltd. in China. Its molecular formula is $C_{16}H_{11}O_4N_2SNa$. The chemical structure of the dye Acid Orange 7 is shown in Fig. 1.

Preparation of the activated zero valent iron by potassium persulphate: The nanoscale zero valent iron was synthesized in the laboratory using a modified method 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 borohydribe solution following the equation below:

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

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, and with vigorous stirring PVP was completely dissolved. The 100 mL 0.06 M potassium borohydribe solution was swiftly added into the
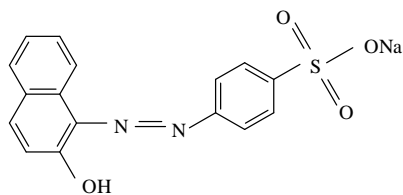
Fig. 1: The chemical structure of the dye Acid Orange 7.

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 100 mL of 2 mmol/L potassium persulphate in the beaker for 50 min at room temperature. They were then washed twice by the deionized distilled water, and dried in the oven at 105°C for 4 hours. The dry activated zero valent iron particles with potassium persulphate were gained and used for the further experiments.

Experimental procedure: Bath experiments were conducted by mixing 100 mL of dye solution and the activated zero valent iron particles in 250 mL Erlenmeyer flasks. The flasks were shaken at 150 rpm and in a contact temperature. All the degradation tests were performed twice, and the average values were used.

Analytical methods: The structures and sizes of the activated zero valent iron particles were characterized by the scanning electron microscopy. The value of pH was measured with a pH probe according to APHA standard method. The concentration of dye Acid Orange 7 was measured with a UV-1600 spectrophotometer at 485 nm.

The degradation rate of dye Acid Orange 7 was calculated as following:

$$Q = \frac{C_0 - C_t}{C_0} \times 100\% \qquad ...(7)$$

Where, C_0 and C_t (mg/L) are the initial and equilibrium concentrations of dye Acid Orange 7 in the solution respectively. Q is the degradation rate of dye Acid Orange 7.

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 significance was noted at $\alpha=0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

The structure of the activated zero valent iron particles: The structures and sizes of the activated zero valent iron particles were characterized by the scanning electron microscopy. The image is shown in Fig. 2.

The image indicated that there were many modular protrusions over the surface. These nodules were the *in-situ* prepared zero valent iron particles. They were spherical in
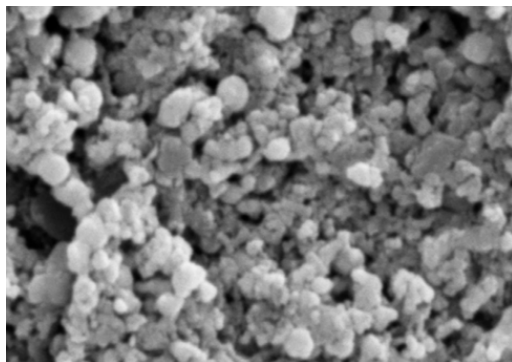
Fig. 2: SEM image of the activated zero valent iron particles.

shape, and distributed throughout the surface of the clays without noticeable aggregation.

The effect of reaction time: The reaction time is an important parameter in the process of reaction. In order to investigate the effect of reaction time on the degradation of azo dye Acid Orange 7 by the activated zero valent iron, the effect of reaction time was studied in a series of experiments. Bath experiments were conducted by mixing 100 mL of 200 mg/L azo dye Acid Orange 7 in aqueous solution, pH 2.0 in aqueous solution and 3 g of the activated zero valent iron particles in 250 mL Erlenmeyer flasks. The flasks were shaken at 150 rpm and in a contact temperature of 303 K. The results of the experiments are shown in Fig. 3.

As shown in Fig. 3, it indicated that the reaction time had an important role in the reaction process of degradation. As the reaction time increased, the degradation rate of azo dye Acid Orange 7 also increased. In the first stage of reaction process, the reaction rate was very quick. Then, the reaction rate of degradation began to increased slowly. The reaction process reached equilibrium in about 10 min. So,
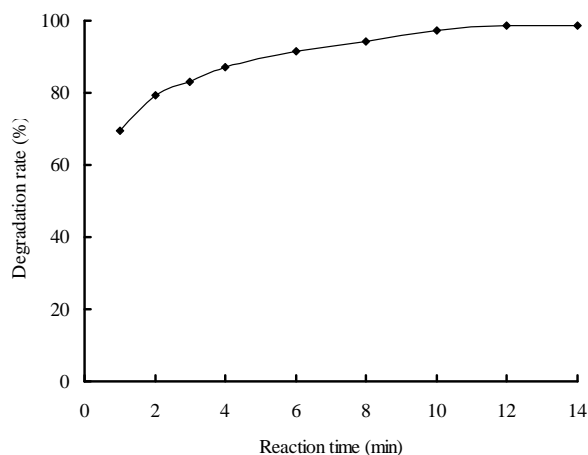
the reaction time of 10 min was thought to be optimum. In the following experiments, the reaction time of 10 min is chosen.

The effect of the activated zero valent iron dosage: The reaction parameter of the activated zero valent iron dosage is very important for the reaction rate. In order to investigate the effect of the activated zero valent iron dosage, a series of experiments were carried out. Bath experiments were conducted by mixing 100 mL of 200 mg/L azo dye Acid Orange 7 in aqueous solution, with reaction time of 10 min and pH 2.0 in 250 mL Erlenmeyer flasks. The flasks were shaken at 150 rpm and in a contact temperature of 303 K. The activated zero valent iron dosage ranged from 1 g to 5 g. The experimental results are shown in Fig. 4. It was found that the degradation rate of azo dye Acid Orange 7 in aqueous solution increased with the increasing of the activated zero valent iron particles. This is because more ·OH radicals are produced with the increase in the activated zero valent iron particles due to Fenton's reaction (Wang et al. 2015).

The effect of pH in solution: The value of pH in aqueous solution is an important parameter affecting azo dye removal no matter what kind of azo dyes they were. The actual dye containing wastewater has a wide range of pH value in aqueous solution, so it is very necessary to investigate the influence of pH in aqueous solution on degradation process. Bath experiments were conducted by mixing 100 mL of 200 mg/L azo dye Acid Orange 7 in aqueous solution, with reaction time of 10 min and 3 g of the activated zero valent iron particles in 250 mL Erlenmeyer flasks. The flasks were shaken at 150 rpm and in a contact temperature of 303 K. The pH in solution ranged from 2.0 to 6.0. The effect of pH in solution on the degradation rate of azo dye Acid Orange 7 is shown in Fig. 5.

It can be seen from the results that the degradation rate of azo dye Acid Orange 7 decreased with an increase in the initial pH from 2.0 to 6.0. These experimental observations can be explained by the effects of pH value in solution on chemistry and Fenton reaction. It was widely reported that higher degradation rates were observed at lower pH value in solution for dye (Chen et al. 2011).

The effect of the reaction temperature: Temperature is one of the important parameters in chemical reactions. It has an important effect on the rate of the reactions. Bath experiments were conducted by mixing 100 mL of 200 mg/L azo dye Acid Orange 7 in aqueous solution, reaction time of 10 min, pH 2.0 in solution and 3 g of the activated zero valent iron particles in 250 mL Erlenmeyer flasks. The flasks were shaken at 150 rpm in the contact temperature. The reaction
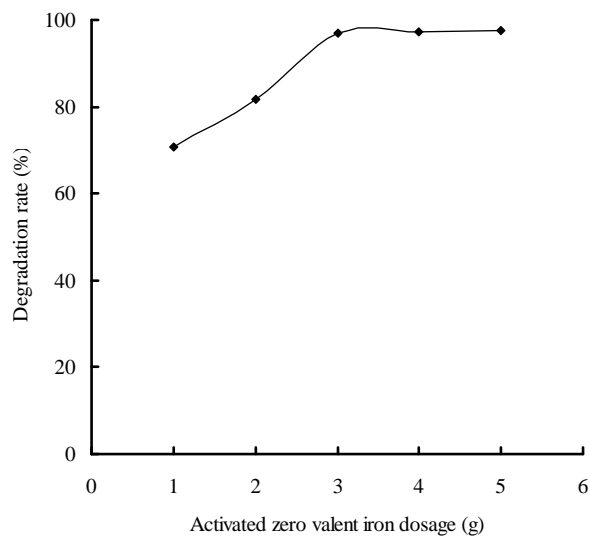

Fig. 3: The effect of reaction time on the degradation rate.

Fig. 4: The effect of activated zero valent iron dosage on the degradation rate.

Fig. 5: The effect of pH in aqueous solution on the degradation rate.

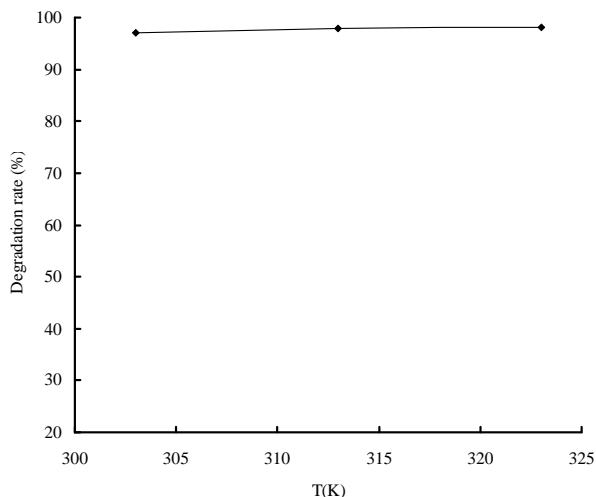Fig. 6: The effect of reaction temperature on the degradation rate.

Fig. 7: The effect of dye concentration on the degradation rate.

temperature ranged from 303 K to 323K. The effect of the reaction temperature is shown in Fig. 6.

From Fig. 6, the experimental results indicated that the degradation rate is affected by the temperature. The degradation rate of azo dye Acid Orange 7 increased with increase in temperature. It also indicated that the degradation process was an endothermic reaction. Mielczarski et al. (2005) have studied the decomposition of azo dye in water in the presence the zero valent iron at pH 4 and 5 over the temperature range from 20 to 50. They claimed that the acceleration of decolorization by raising temperature resulted from the different types of corrosion products on the
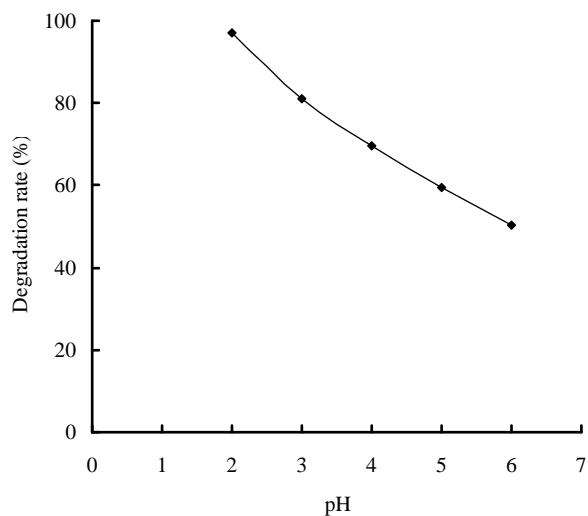
surface of zero valent iron. Corrosion of zero valent iron could increase the surface area significantly. They reported tat the decolorization reaction was controlled by the kinetics of surface process. Based on the above results, it is concluded that surface reactions, including sorption and chemical reaction, controlled the rate.

The effect of the initial concentration of azo dye: The effect of the initial concentration of azo dye Acid Orange 7 in aqueous solution on the degradation rate was evaluated at a concentration range from 100 mg/L to 400 mg/L. Batch experiments were conducted by mixing 100 mL of azo dye Acid Orange 7 in aqueous solution, reaction time of 10

min, pH 2.0 and 3 g of the activated zero valent iron particles in 250 mL Erlenmeyer flasks. The flasks were shaken at 150 rpm in a contact temperature of 303 K. The initial concentration of azo dye ranged from 100 mg/L to 400 mg/L.

Fig. 7 showed that the degradation rate of azo dye Acid Orange 7 was affected by the initial dye concentration. It can be seen that the degradation rate of azo dye Acid Orange 7 decreased with the increasing of the initial concentration of azo dye.

CONCLUSIONS

In this study, the synthetic zero valent iron was activated by potassium persulphate. The degradation of azo dye Acid Orange 7 by potassium persulphate activated using zero valent iron was carried out. The effect of several parameters, such as the pH in solution, the reaction time, reaction temperature, the activated zero valent iron amount and the initial concentration of dye on the removal process was investigated. The results showed that the degradation rate of azo dye Acid Orange 7 by the activated zero valent iron was high. The operation parameters had an important effect on the degradation of azo dye Acid Orange 7 in aqueous solution.

ACKNOWLEDGEMENTS

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