



Degradation of Dye C.I. Reactive Red 15 in Aqueous Solution by Kaolinite Supported Zero Valent Iron

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ABSTRACT

Dyes are important source of water pollution and their degradation products may be carcinogens and toxic to mammals. For evaluation of oxidative degradation of dye wastewater, the kaolinite supported zero valent iron were synthesized. The surface morphology of kaolinite and kaolinite supported zero valent iron were observed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The degradation of dye C.I. Reactive Red 15 in aqueous solution by kaolinite supported zero valent iron was investigated in details. The effects of the dosage of kaolinite supported zero valent iron, pH in solution, reaction time and the initial dye concentration on the degradation were studied. The results showed that the pH value, the dosage of kaolinite supported zero valent iron and the initial dye concentration had an important impact on dye degradation. Under these conditions, such as 80 mg/L dye C.I. Reactive Red 15, 20 min of reaction time, 0.5 g kaolinite supported zero valent iron particles, pH value of 2.0, temperature of 308 K and 120 rpm respectively, the degradation rate of dye C.I. Reactive Red 15 reached 82.3%.

INTRODUCTION

Effluents of textile industries are highly coloured and disposal of these wastes into receiving waters causes drastic damages to the environment (Forgacs et al. 2004). Indeed, the presence of dyes in textile effluents can pose a serious environmental menace when they are discharged into the environment without previous treatment or with an insufficient level of treatment. They may significantly affect photosynthetic activity and also be toxic to some aquatic life due to the presence of metals, chlorides, etc. (Santos et al. 2007, Gupta & Suhas 2009). Most of the dyes released during textile clothing, printing and dyeing processes are considered as hazardous and toxic to some organisms and may cause direct destruction of aquatic creatures (Guz et al. 2014). In addition, dye wastewaters are commonly characterized by high salts content and low biodegradation potential, which makes effective removal by conventional wastewater treatment processes difficult. Treatment will, therefore, be essential to remove these dyes, which are harmful to the environment. Therefore, the dye removal from textile wastewater is a great challenge, and a significant amount of research has been devoted to colour removal from textile effluents.

Many decolorization processes have been applied, but not all processes work well for all coloured wastewaters (Hao et al. 2000). Physical processes, such as membrane separa-

tion, removed up to 99% of a variety of reactive dyes in laboratory studies (Wu et al. 1998) and were successful in a pilot scale study (Chen et al. 1997). However, most physical processes are typically used at low flow rates due to cost, membrane fouling and flux decline, and the resulting high-salt content concentrate requires further treatment (Hul et al. 1997). Conventional aerobic biological treatment processes are ineffective against dyes (Beydilli et al. 2000). The major colour removal mechanism is adsorption to the solids, but reactive dyes adsorb poorly due to their high aqueous solubility. Anaerobic biological processes have the capacity to reductively decolorize dyes, but anthraquinone dyes are inhibitory to methanogenic systems (Lee & Pavlostathis 2004).

Use of zero valent iron for dye decolorization is growing because of its abundance, low toxicity, low cost and effectiveness as a reducing agent (William et al. 2008). The zero valent iron reductive transformation is believed to be surface-mediated and is coupled with the oxidation/corrosion of zero valent iron to Fe^{2+} , while two electrons are released. The reduction mechanism involves several steps: diffusion to metal surface, adsorption to the metal surface, transfer of electrons from the metal surface to the adsorbed contaminant resulting in chemical reduction, desorption of products, and diffusion of products to the bulk solution (Matheson & Tratnyek 1994, Qiu et al. 2015).

Clays are defined as fine grained minerals, which may be plastic in nature, clays can be hardened when dried or fired and they contain appropriate water contents (Hajjaji et al. 2016). Clay generally contain phyllosilicates, however, the other contents present may impart either plasticity or harden when fired or dried. Clay can be differentiated from other fine grained soils by their difference in minerology and size. Besides, the clay possesses large surface area, which contributes to its high adsorption capacity (Hassan & Hameed 2011). There are many types of clays expected to have the highest adsorptive capacity in comparison to others (Ramirez et al. 2007). Further, clay could be modified to enhance its efficiency for the removal of pollutants from water and wastewaters (María et al. 2008).

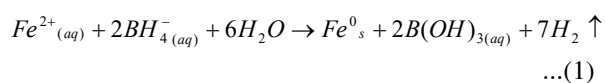
The zero valent iron has the advantage that the small particle size results in a large specific surface area and great intrinsic reactivity of surface sites. However, the zero valent iron nanoparticles tend to either react with surrounding media or agglomerate, resulting in significant loss of reactivity. To prevent particle aggregation, a wide variety of stabilizers have been proposed to modify zero valent iron particle surface characteristics. More recently, clay supported zero valent iron have been researched and applied into the treatment of dye wastewater (Djurđja et al. 2014).

In this work, the kaolinite supported zero valent iron was synthesized. The surface morphology of kaolinite and kaolinite supported zero valent iron were observed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Then, the degradation of dye C.I. Reactive Red 15 in aqueous solution by kaolinite supported zero valent iron was investigated in detail.

MATERIALS AND METHODS

Materials: The dye 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 C.I. Reactive Red 15 is shown in Fig.1. The kaolinite was purchased from Shanghai Chemical Co. Ltd. in China and was crushed to obtain clay with a diameter less than 50 μm .

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



20 g zero valent iron and 20 g kaolinite were added to 500 mL deionized water and mixed for 2 h with a magnetic stirrer. The mixture was centrifuged and dried at 105°C, powdered to pass through a 100-mesh screen and the kaolinite supported zero valent iron was obtained.

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 kaolinite supported zero valent iron and 100 mL of dye C.I. Reactive Red 15 with initial concentrations in aqueous solution. The pH of 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:

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

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.

The surface morphology of kaolinite and kaolinite supported zero valent iron was observed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Statistical analyses of data: All the experiments were repeated in duplicate and the results were represented as the mean \pm 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 the standard deviation of means (mean \pm SD). All the statistical significances were noted at $\alpha=0.05$ unless otherwise specified.

RESULTS AND DISCUSSION

Characterization of kaolinite supported zero valent iron: The morphology and nanoparticle distribution of zero valent iron and kaolinite supported zero valent iron were analysed by SEM and TEM. The observed results are shown in Fig. 2 and Fig. 3.

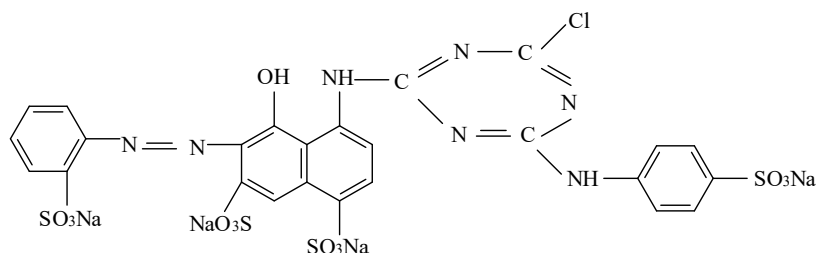


Fig.1: The chemical structure of the C.I. Reactive Red 15.

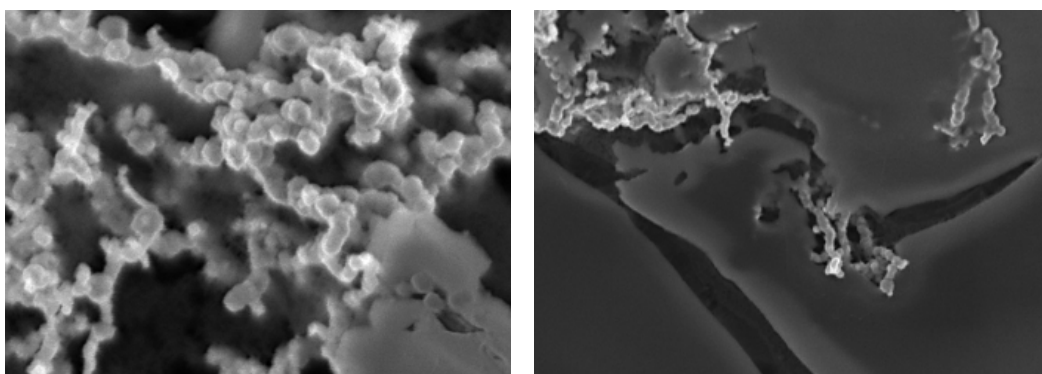


Fig. 2: SEM images of laboratory synthesized zero valent iron (left) and kaolinite supported zero valent iron particles (right).

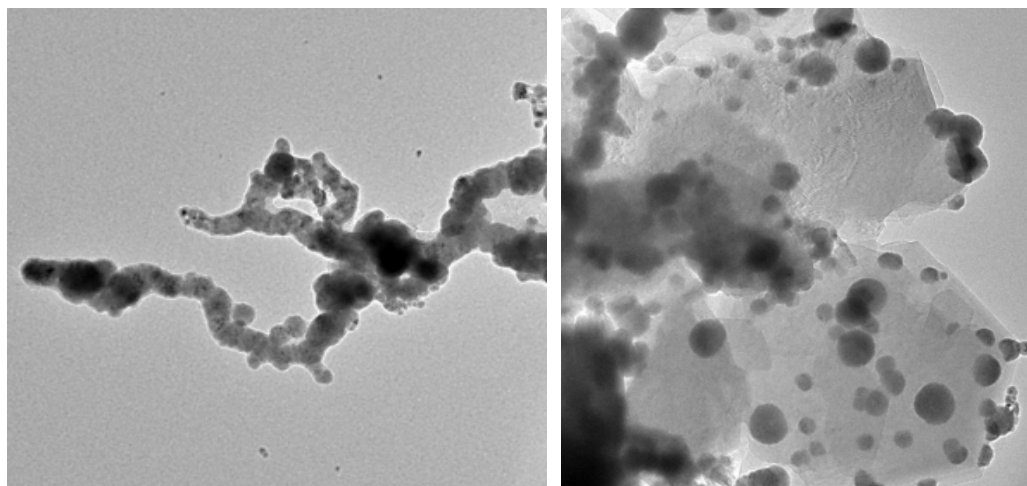


Fig.3: TEM images of laboratory synthesized zero valent iron (left) and kaolinite supported zero valent iron particles(right).

As shown in Fig. 2, there are many nodular protrusions over the surface. These nodules were the Fe^0 particles. They were spherical in shape, and were distributed throughout the surface of the kaolinite without noticeable aggregation.

As shown in Fig. 3, the chain-like aggregates of bare zero valent iron particles were observed. The kaolinite supported zero valent iron particles were clearly discrete and

well dispersed in the kaolinite carriers without aggregation. The obtained particles are close to spherical.

Effect of reaction time: The effect of reaction time on the degradation of dye C.I. Reactive Red 15 was tested by determining the dye concentration every minute. The degradation experiments were carried out under these operational parameters, such as pH value of 2.0, 60 mg/L dye C.I. Reac-

tive Red 15, 0.5 g kaolinite supported zero valent iron particles, temperature of 308 K and 120 rpm. The results are shown in Fig. 4.

Fig. 4 shows that the degradation rate of dye C.I. Reactive Red 15 increased with the reaction time. At first stage of 6 min, the degradation rate increased very quickly. After 8 min, the degradation rate increased slowly and reached equilibrium. It also indicated that the reaction process appeared very quickly. The degradation of dye C.I. Reactive Red 15 reached 83.5% at 20 min. In the following experiments, the reaction time of 20 min was chosen.

Effect of pH in solution: The effect of pH in solution on the degradation of dye C.I. Reactive Red 15 was studied in the pH range of 2.0 and 12.0. The other parameters were 20 min of reaction time, 60 mg/L dye C.I. Reactive Red 15, 0.5 g kaolinite supported zero valent iron particles, temperature of 308 K and 120 rpm. The experimental results are shown in Fig. 5.

From Fig. 5, 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 dye C.I. Reactive Red 15 decreased with increasing the value of pH in solution. The results indicated that the value of pH in solution played a very important role in the degradation of dye C.I. Reactive Red 15 by kaolinite supported zero valent iron. Apparently, the degradation processes were acid driven for dye C.I. Reactive Red 15. The possible reason might be that the kaolinite supported 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 decreased (Nathalie et al. 2017).

Effect of the dosage of kaolinite supported zero valent iron: The experimental conditions are 20 min of reaction time, 60 mg/L dye C.I. Reactive Red 15, pH value of 2.0, temperature of 308 K and 120 rpm. Fig. 6 shows the effect of the dosage of kaolinite supported zero valent iron on the degradation of dye C.I. Reactive Red 15.

As shown in Fig. 6, the degradation rate increased with the increase of the dosage of kaolinite supported zero valent iron. The dosage of kaolinite supported zero valent iron had an important role on the degradation rate of dye C.I. Reactive Red 15.

Effect of the initial dye concentration: The influence of various initial dye C.I. Reactive Red 15 concentrations on the degradation process was carried out between 20 and 100 mg/L. The other parameters were 20 min of reaction time, 0.5 g kaolinite supported zero valent iron particles, pH value of 2.0, temperature of 308 K and 120 rpm. Fig. 7

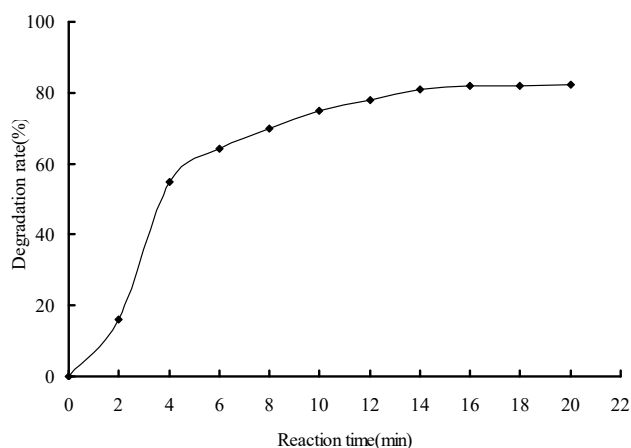


Fig. 4: Effect of reaction time on the degradation of dye C.I. Reactive Red 15.

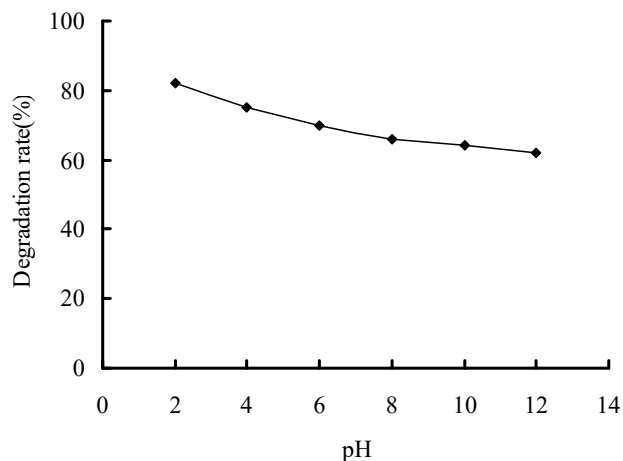


Fig. 5: Effect of pH in solution on the degradation of dye C.I. Reactive Red 15.

shows the effect of the initial dye concentration on the degradation process.

From Fig. 7, the degradation rate decreased with the increase of initial dye concentration. The degradation rate reached 82.3% under the following operating parameters, such as 80 mg/L dye C.I. Reactive Red 15, 20 min of reaction time, 0.5 g kaolinite supported zero valent iron particles, pH value of 2.0, temperature of 308 K and 120 rpm respectively.

CONCLUSIONS

In this work, the degradation of dye C.I. Reactive Red 15 in aqueous solution onto kaolinite supported zero valent iron was carried out in detail. The transmission electron

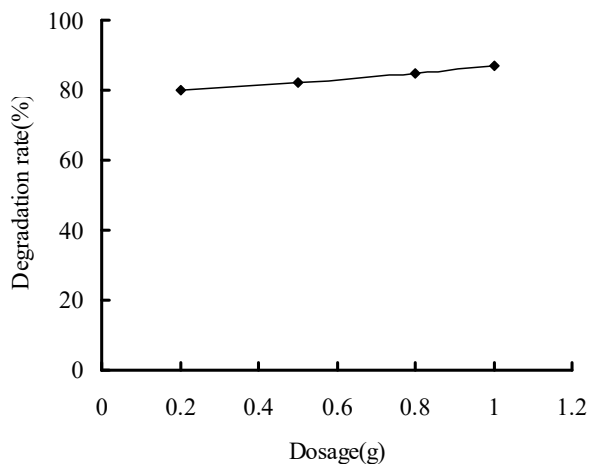


Fig.6: Effect of the dosage of kaolinite supported zero valent iron on the degradation of dye C.I. Reactive Red 15.

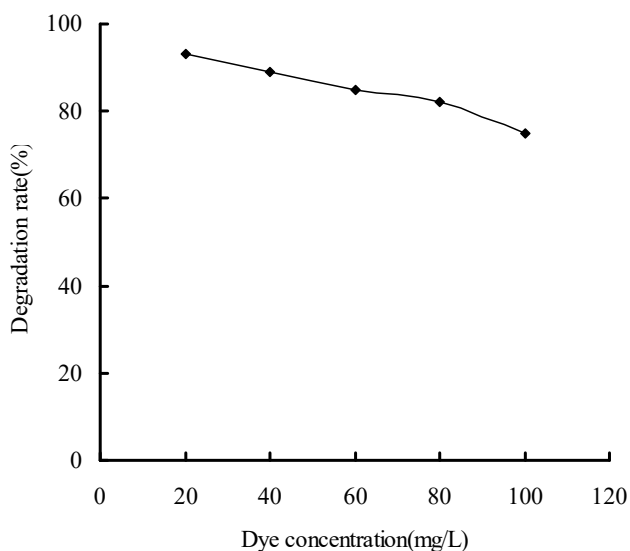


Fig.7: Effect of initial dye concentration on the degradation of dye C.I. Reactive Red 15.

microscopy (TEM) and scanning electron microscopy (SEM) were used to characterize the structure of kaolinite supported zero valent iron. The results showed that the pH value, the dosage of kaolinite supported zero valent iron and the initial dye concentration had an important effect on the dye degradation. The degradation rate reached 82.3% under the following operating parameters, such as 80 mg/L dye C.I. Reactive Red 15, 20 min of reaction time, 0.5 g kaolinite supported zero valent iron particles, pH value of 2.0, temperature of 308 K and 120 rpm.

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