Reusability of Iron sludge as an Iron source for Fenton-type process[*]

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As one of the hazardous solid wastes, iron sludge has received considerable and increasing attention for its potential damage to the environment. Thus this paper reports the reusability of iron sludge for a Fenton-type process. However, the slow transformation of Fe(III)/Fe(II) limits its repetitive and widespread application. Hence, hydroxylamine (HA), a common reducing agent, was introduced to iron-sludge/H_2O_2 system to accelerate the conversion of Fe(III)/Fe(II). With the addition of HA, orange G (OG) degradation was largely increased at pH 2.0-9.0, and the generation of hydroxyl-radicals was significantly promoted. It was surprised to find that the catalytic ability of iron sludge maintained constantly in the ten consecutive runs with 100% iron recovery. Thus the present study provides a promising way to reuse iron sludge for the rapid degradation of refractory organics and dispose the solid iron-based wastes.

Keywords: Iron sludge; Fenton; NH_2OH; Hydroxyl radical; Heterogeneous catalysis

1. Introduction

Fenton process has been extensively and successfully studied for the effective treatment of industrial wastewater[1]. However, it has a few significant disadvantages: (i) handling dangerous H_2O_2 and (ii) high costs of disposing iron sludge. To minimize this disposal, two approaches have been discussed: (a) development of heterogeneous catalysts and (b) reuse of iron sludge. In the former, the catalytic activity of heterogeneous catalysts usually deteriorates with the repeated use of the catalysts because of the leaching of active iron or the decay of active catalytic sites. In the latter, iron sludge is reused as a coagulant for water treatment and as an iron source for Fenton reaction. The input of

regenerated Fe^{3+} to the classic Fenton reactor after re-dissolution of iron sludge by acid is simple but Fe^{3+} must be reduced to Fe^{2+} by H_2O_2 in the reactor, resulting in an increasing chemical cost of H_2O_2. Kavitha and Palanivelu [2]recycled iron sludge for the classic Fenton process after sludge re-dissolution through the addition of acid and HA, in which Fe^{3+} ions in the sludge are reduced to Fe^{2+} ions by reaction with HA. But can the iron sludge used in the solid form? What is its performance in Fenton process? What is the role of HA in Fenton process?

Therefore, solid iron sludge was introduced into Fenton as an iron source in this paper to (i) explore the role of HA, (ii) evaluate the effects of HA and H_2O_2dosage, and initial pH on the performance of HA/Fenton, and (iii) examine the stability of iron sludge in consecutive runs.

2. Methods and Materials

2.1. *Materials*

Hydrogen peroxide (30%), hydroxylamine (NH_2OH, 99.9%), orange G (OG, 99.5%) and Tert-butyl alcohol (TBA)were of analytical reagent grade. 5,5-dimethyl-1-pyrolin-N-oxide (DMPO) were of ACS reagent grade and supplied by J&K Chemical. The iron sludge was obtained from a typical Fenton process.

2.2. *Experimental procedure*

All experiments were performed in 500 mL borosilicate glass jars with a constant stirring rate at 25°C. Each 500 mL reaction solution with desired concentrations of OG, iron sludge and HA, was prepared with ultrapure water and adjusted to the desired pH. The desired H_2O_2 dosage was then added to start the reaction. Samples were withdrawn at predetermined time intervals and quenched with excess pure TBA before analysis. The OG was quantified with an UV-vis spectrometer at 478 nm (Jingke, UV760CRT).

3. Results and Discussion

3.1. *Role of HA*

The removal of OG by H_2O_2 alone and HA/H_2O_2 was negligible and that by iron sludge was less than 18% in 60 min (data not shown). As can be seen in Figure 1(a), less than 20.4% of OG was degraded in 60 min by Fenton process. Such low degradation efficiency in Fenton process could be interpreted with the limited Fe(II) sites on iron sludge and the slow transformation from Fe(III) to Fe(II). Surprisingly, with the addition of 10 mM HA, more than 99% of OG was

degraded in 60 min. It could be inferred that the addition of HA into Fenton process might greatly accelerate the cycle of Fe(III)/Fe(II) and the generation of reactive radicals [3].
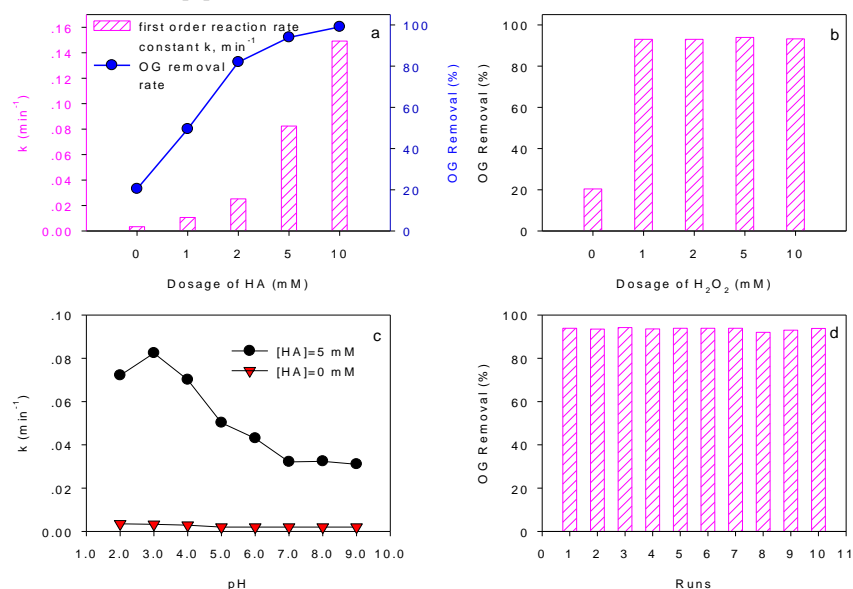

Fig. 1. Effects of (a) HA dosage, (b) H_2O_2 dosage, and (c) pH on the degradation of OG by Fenton process; (d) stability of iron sludge in ten consecutive runs.Reaction conditions: (a) [OG]=0.1 mM, [H_2O_2]=5.0 mM, [iron sludge]=0.1 g L^{-1}, pH=3.0, 25 ℃; (b) [OG]=0.1 mM, [HA]=5.0 mM, [iron sludge]=0.1 g L^{-1}, pH=3.0, 25 ℃; (c)[OG]=0.1 mM, [H_2O_2]=5.0 mM, [iron sludge]=0.1 g L^{-1}, 25 ℃; (d) [OG]=0.1 mM, [H_2O_2]=5.0 mM, [HA]=5 mM, [iron sludge]=0.1 g L^{-1}, pH=3.0, 25 ℃;. Reaction time is 60 min for all the experiments.

3.2. *Effect of HA and H_2O_2 dosage*

As shown in Figure 1(a), increased degradation of OG was observed with increasing HA concentration from 1 to 10mM. It should be noted that HA mainly existed in the form of NH_3OH^+ at pH 3.0 with pK_{a1}=5.96. The degradation of OG was actually regulated by NH_3OH^+ with the addition of HA into Fenton process. Although increased NH_3OH^+ concentration could accelerate the conversion of Fe(III)/Fe(II), the reasonable amount of generated ROS might be quenched by excess NH_3OH^+ (k<5.0×10^8 M^{-1} s^{-1} for •OH[4]).

The effect of variable H_2O_2 concentration on the degradation of OG was studied in HA/Fenton process, as shown in Figure 1(b). The increased dosage of H_2O_2 from 1 to 10mM had no effect on the kinetics of OG degradation, which indicated that the availability of H_2O_2 was not the limiting factor controlling the yield of radicals.

3.3. *Effect of pH*

As shown in Figure 1(c), OG degradation by Fenton or HA/Fenton process exhibited strong pH dependent. Without HA, the apparent first-order rate constant (k, min^{-1}) decreased linearly from 3.50×10^{-3} to $1.99 \times 10^{-3} min^{-1}$ as pH increased from 2.0 to 9.0,while the addition of HA greatly improved OG removal. With initial pH increasing from 2.0 to 3.0 in the presence of HA, OG removal was promoted due to the formation of $Fe(OH)_2$, which has been reported to be more reactive than Fe(II) ions due to the presence of –OH groups [5]. As pH increased from 3.0 to 9.0, the degradation of OG was sharply dropped from 8.24×10^{-2} to $3.10 \times 10^{-2} min^{-1}$. This can be attributed to the species distribution of HA at different pH. As pH increased from 3.0 to 9.0, the fraction of NH_2OH gradually becomes the dominant existing form of HA. Hence, a considerable amount of generated radicals would be consumed by HA at near neutral pH ($9.5 \times 10^9 M^{-1} s^{-1}$ for •OH[4]).

3.4. *Stability of iron sludge*

The effect of HA on the stability of iron sludge was investigated by reusing it in ten successive runs under the same reaction conditions and the results are shown in Figure 1(d). OG was totally decomposed with 100% iron recovery during the ten runs due to the presence of HA, indicating the regeneration of Fe(II) sites by HA.

4. Conclusion

The applicability of catalytic treatment technologies for azo dye treatment was evaluated by HA enhanced Fenton process. The addition of HA into Fenton process greatly accelerated the cycle of Fe(III)/Fe(II) and the generation of reactive •OH. The stability of iron sludge was satisfied in HA/Fenton process with no activity loss in the consecutive runs.

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