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Reuse of Ferric Sludge by Ferrous Sulfide in the Fenton Process for Nonylphenol Ethoxylates Wastewater Treatment

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Abstract

In this paper, Fenton process was determined to be an effective technique to treat the refractory nonylphenol ethoxylates (NPEOs) wastewater. The chemical oxygen demand (COD) removal efficiencies above 89% were obtained when the initial COD concentration was 12,000 mg/L. However, a large amount of ferric sludge (SS = 8.724 g/L) would be produced after the Fenton oxidation of the wastewater and must be disposed appropriately. A novel process for Fenton sludge reused by low-cost ferrous sulfide (FeS) was also investigated. Experimental results show that the Fenton sludge could be reduced to produce a certain amount of Fe^{2+} in the acidic mixed liquor by FeS. This mixed liquor from Fenton sludge could be used as the new catalyst in the Fenton process and was also highly effective for the NPEOs wastewater treatment. The residual FeS from the mixed liquor could be used for the next batch of the reaction.

Keywords

Fenton Process, Iron-Containing Sludge, Ferrous Sulfide, Sludge Reused, Nonylphenol Ethoxylates

1. Introduction

The Fenton process has been extensively studied and successfully used for the treatment of various industrial wastewaters. For example, the Fenton process can be used to treat highly loaded, refractory and toxic wastewaters which cannot be biologically treated [1] [2] [3]. However, despite its simplicity, the main weakness of the Fenton process is the formation of sludge during neutralization after Fenton oxidation. The yield of Fenton sludge is dependent upon the ratio and volume of the added reagents. Due to the residual of toxic organics or heavy metals in it, sludge from the Fenton process treating recalcitrant industrial wastewater is often disposed as hazardous solid waste, which leads to high sludge disposal cost and the risk of secondary pollution. Therefore, Fenton sludge is the main obstacle preventing full scale application of the Fenton process in the field of industrial wastewater treatment [4].

To minimize the above-mentioned sludge formation, two approaches have been investigated: development of heterogeneous catalysts and the reuse of the iron-containing sludge.

Various heterogeneous catalysts have been developed, such as natural minerals [5], iron-containing clays [6], iron immobilized on solid support [7] and zero-valent [8] [9]. Heterogeneous catalysts are superior to the traditional homogeneous catalyst, due to the easy separation of the catalysts from the treated wastewater by sedimentation or an external magnetic field. Therefore, generation of Fenton sludge in a heterogeneous Fenton system can be reduced to some extent. However, the catalytic activity is usually deteriorated after repetitive use due to the leaching of active iron or the decay of active catalytic sites, notably in acidic condition [10].

During the Fenton treatment of wastewater, the oxidation and coagulation of ferric hydroxy complexes both contribute to the removal of the organic compounds. Therefore, the complete elimination of the coagulation step may be undesirable when a high overall process efficacy is desired. Recently, reuse of Fenton sludge has been drawing increasing interest from researchers. The reuse of iron-containing sludge as an iron source for the synthesis of a new Fenton catalyst has been reported [11]. And the sludge can also perform as Fenton catalyst after chemical regeneration with reducing agent such as hydroxylamine hydrochloride [12]. Juri *et al.* [13] suggested the reuse of ferric sludge without any regeneration as an iron source in the Fenton-based process displayed as a feasible solution to minimize the production of hazardous sludge waste and reduce the overall cost of the treatment process.

Ferrous sulfide (FeS), the main component of pyrrhotite, is a kind of common iron minerals in the soil environment. In strongly acidic solution, FeS may dissolve into Fe^{2+} and sulfide (S^{2-}) (Equation (1)), and S^{2-} tends to transform into HS^- and H_2S in acidic solution (Equations (2) and (3)). H_2S may reduce Fe^{3+} to Fe^{2+} (Equation (4)) [14]. Thereby, in theory, the iron-containing sludge can be reduced to Fe^{2+} by FeS as the catalyst for Fenton process in acidic solution.

$$FeS \rightarrow Fe^{2+} + S^{2-} \quad (1)$$

$$S^{2-} + H^+ \rightarrow HS^- \quad (2)$$

$$HS^- + H^+ \rightarrow H_2S \quad (3)$$

$$2Fe^{3+} + H_2S \rightarrow 2Fe^{2+} + S\downarrow + 2H^+ \quad (4)$$

Nonylphenol ethoxylates (NPEOs) are non-ionic surfactants that have been confirmed endocrine disruptors. They are not completely biodegradable under normal environmental conditions and would product of a large amount of foam to disturb the normal running in aeration [15] [16]. Therefore, the NPEOs wastewater needs to be disposed by other technologies such as Fenton oxidation.

In this work, a new reuse method for Fenton sludge by FeS was investigated. At first, the reactions of classic Fenton's reagent with high concentration NPEOs wastewater had been evaluated. Then the Fenton sludge was reduced to produce a new catalyst for Fenton process in NPEOs wastewater treatment.

2. Experimental

2.1. Chemicals

The NPEOs wastewater was obtained from a chemical enterprise in China. It is a refractory wastewater with high chemical oxygen demand (COD) (12,000 ± 500 mg/L) and its pH was about 6.5. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (China).

2.2. Characterization of Fenton Sludge

The iron-containing sludge derived from the Fenton process was characterized as follows. The water content and total solid content of the iron-containing sludge was 89% and 11%, respectively. The total suspended solids (TSS) was found to be 8.724 g/L, and the volatile suspended solids (VSS) was found to be 6.732 g/L, indicating the presence of abundant organics in the sludge. The total iron content of the sludge was as high as 1.4 g/L ± 0.2 g/L.

2.3. Analytical Methods

The COD of Fenton sludge and effluent were measured by the standard potassium dichromate method. The total iron content of the Fenton sludge and total iron leaching were determined by the phenanthroline method according to Standard Methods.

2.4. Experimental Procedure

The Fenton process was started when the required $FeSO_4$ dosage was added into the beaker containing 100 mL NPEOs wastewater. Meanwhile, the intermixture was stirred by a magnetic stirrer with a desired stirring speed. In addition, the initial pH of NPEOs was adjusted by adding diluted sulfuric acid (1 mol/L) or sodium hydroxide solutions (1 mol/L), then quickly added quantitative H_2O_2. Finally, at the selected time stopped the reaction with $Na_2S_2O_3$, and COD of the effluent of each batch experiment was measured.

The dissolution of FeS in acid solution had been investigated before the iron-containing sludge reduction with FeS. The experiments started when the required FeS dosage added into the beaker containing 100 mL required acid aqueous solution. Meanwhile, the intermixture was stirred by magnetic stirrer with desired stirring speed. And the concentration of ferrous ion was measured after filtration by 0.45 μm Syringe-driven Filter.

The procedure of reusing ferric sludge in the Fenton process for NPEOs wastewater treatment was shown in Figure 1. The NPEOs wastewater solution was raised to pH > 7.0 with NaOH after Fenton oxidation process to precipitate iron-containing sludge. The sludge was separated from the solution by decantation and was dissolved in acidic conditions followed by reduction with FeS. The mixed liquor from Fenton sludge was used as the new catalyst in the next Fenton process without any sludge discharge. The residual FeS from the mixed liquor could be used for the next batch of the reaction.

3. Results and Discussion

3.1. Fenton Process

In order to determine the optimal conditions, orthogonal experiment and single factor experiments were analyzed. And the results were H_2O_2 dosage of 76.32 mmol/L, molar ratio of H_2O_2/Fe^{2+} of 3, pH value of 5. Under the optimum operation conditions, the COD removal efficiency was expressed in Figure 2.

As can be seen from Figure 2, about 50% of the COD of the NPEOs wastewater was degraded in 30 minutes of the reaction. Then the COD removal increases significantly with the reaction time and stabilized at 89% in 2 h. In this Fenton experiment, when the initial COD concentration was 12,000 mg/L.

In this study, the efficiency of COD removal were still high in the initial pH of 5. But the pH of all effluents after Fenton process was less than 3. This showed that the pH of the wastewater was decreasing in the reaction process which may be due to the production of some intermediate products, such as nonylphenoxy carboxylic acids (NPEC)

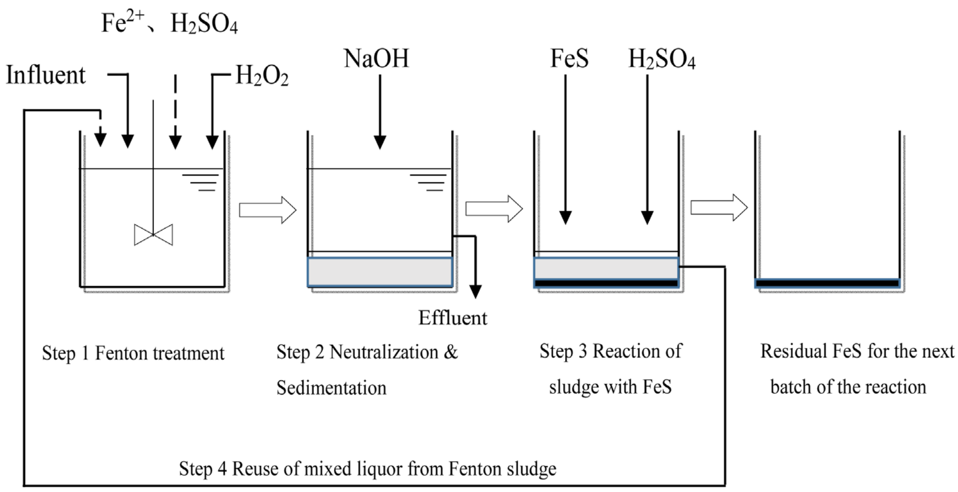

Figure 1. Schematic diagrams of Fenton process with reuse of ferric sludge.

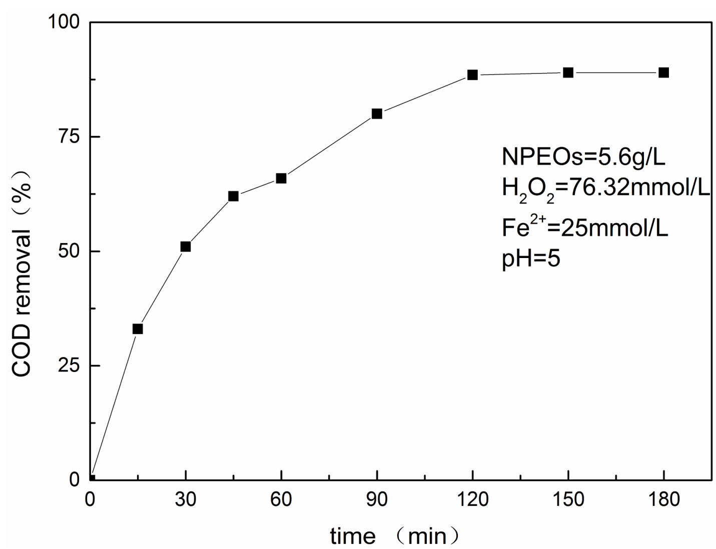

Figure 2. COD removal of the NPEOs wastewater by the Fenton process.

[17] [18]. It was speculated that the optimal pH in reaction process was still in the range of 3 - 4, which was coincident with the values reported in the literatures [19] [20].

3.2. Effect of pH and Dosage on Solubility of FeS

When FeS particle was added to acid aqueous solution, rotten eggs smell generated in a short time, and the color of the solution changed from colorless to light green in 30 s. The effect of pH on solubility of FeS was shown in Figure 3. And the effect of dosage of FeS on solubility of FeS was shown in Figure 4.

As can be seen from Figure 3, only less 10% of FeS dissolved in the acid aqueous solution within 4 h when the pH ≥ 3. When the pH = 2, 23% of FeS dissolved and 141 mg/L ferrous ion generated in the aqueous solution. The amount of dissolved FeS increased with the reaction time increasing whatever the pH was in the solution. When the pH = 2, the FeS dissolution rate is fast because of the enough H^+ in the solution.

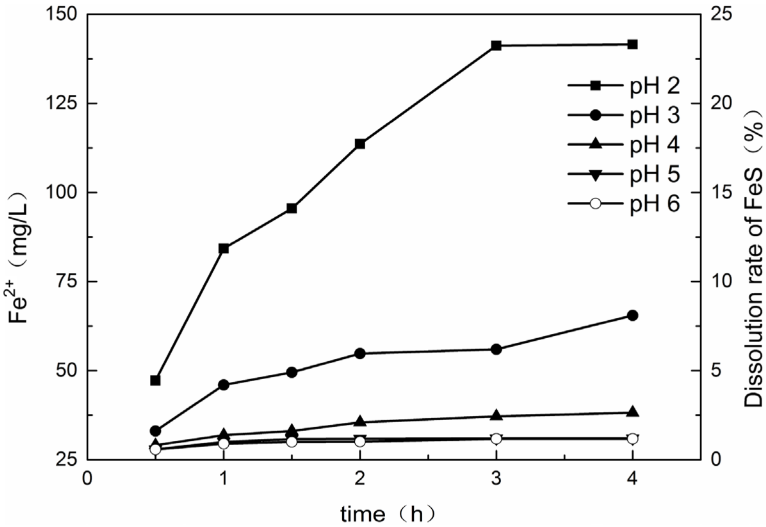

Figure 3. The effect of pH on solubility of FeS.

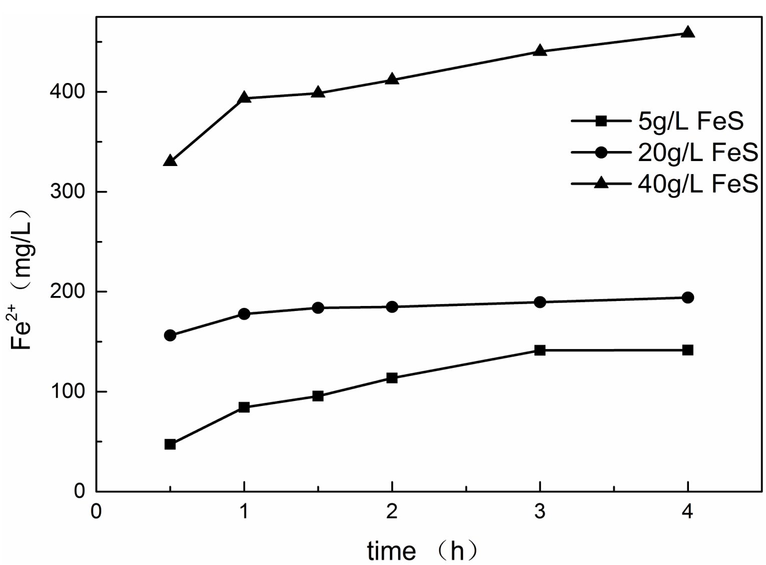

Figure 4. Effect of dosage on solubility of FeS (pH = 2).

And as can be seen from Figure 4, the concentration of ferrous ion kept an increasing with increase of the dosage of FeS, and 25% - 30% of FeS had dissolved no matter the dosage of FeS was 5 g/L, 20 g/L, or 40 g/L.

3.3. The Iron Reusability Studies

According to the results of solubility of FeS in the aicd solution, selected the dosage of FeS was 5 g/L, 25 g/L and 50 g/L to reduce the iron-containing sludge, respectively. The concentration of iron ion generated in the solution and COD removal with the reduced sludge as catalyst in Fenton process were shown in Figure 5.

As can be seen from Figure 5, when the dosage of FeS is 5 g/L, 25 g/L and 50 g/L, the concentration of ferrous ion in the reaction mixture is 140.7 mg/L, 278.1 mg/L and 367.6 mg/L, respectively. It shows that the concentration of ferrous ion still keep an increasing trend in the iron-containing sludge with a slow growth rate. This could be seen from the Equations (1)-(4), the Fe^{2+} from dissolution of FeS and the deoxidization of Fe^{3+} make the concentration of ferrous iron ion trend a balanced concentration in the whole mixed liquor. Besides, the concentration of ferric ion just increases slightly. It shows that the dissolution rate of FeS in the mixture solution is smaller, that is to say the Equation (1) is inhibited by the Fe^{2+} from the deoxidization of Fe^{3+}-containing sludge. An interesting phenomenon is that the Fe^{2+}/Fe^{3+} ratio become high with the increase of the dosage of FeS.

We reuse all the mixed liquor after reaction with FeS as catalyst for the Fenton process in NPEOs wastewater treatment, the reaction condition is same as the first Fenton process except the molar ratio of H_2O_2/Fe^{2+}. And The COD removal is shown in Figure 5 (the line graph). By the calculation, the molar ratio of H_2O_2/Fe^{2+} in the second Fenton process is different from molar ratio of H_2O_2/Fe^{2+} in the first Fenton process. Even so, the COD removal efficiency is as good as the first time. It might be because of the presence of the escaping FeS fine particles and the iron-containing sludge, prompting the Fenton-like process in the whole reaction system. On the whole, all the iron-containing sludge is disposed and reused in the Fenton process.

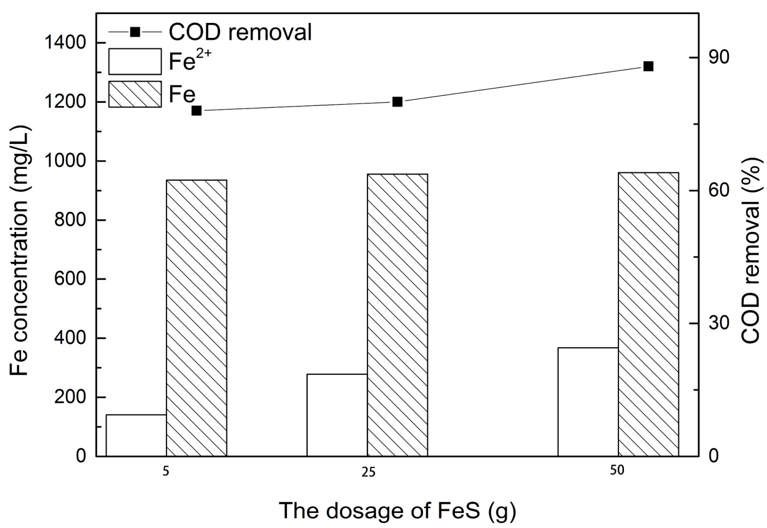

Figure 5. The studies of iron reusability and COD removal.

4. Conclusions

The Fenton process was determined to be an effective technique to treat NPEOs wastewater. Under the optimum operation conditions, the COD removal was 89%.

The Fenton sludge could be reduced to produce a certain amount of Fe^{2+} in the acidic mixed liquor by FeS and this mixed liquor could be used as the new catalyst in the Fenton process without any sludge discharge. The COD removal of the NPEOs wastewater was nearly 80%. After proper regulation, the new method of reducing Fenton sludge could be used in the actual industry totally. And the reaction devices and the treatment of excess H_2S should be further explored.

Acknowledgements

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