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Degradation of phenol from aqueous solution using waste blast furnace flue dust and hydrogen peroxide

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ABSTRACT

A novel method to degrade phenol from simulated wastewater was studied using waste blast furnace flue dust with hydrogen peroxide (H_2O_2). The factors that affect the degradation efficiency, including the pH of the solution, the initial H_2O_2 concentration, the amount of blast furnace flue dust, the reaction temperature, and the reaction time, were studied. The experimental results show that 1,000 mg/L of phenol in simulated wastewater can be decomposed completely within 12 h by 15 g/L blast furnace flue dust with 30 mmol/L H_2O_2 in a solution whose pH was 3.0 at the temperature of 35℃. The mechanism of phenol degradation was also investigated by high-performance liquid chromatography, X-ray diffraction, and UV–vis spectrum.

Keywords: Blast furnace flue dust; Phenol; H_2O_2; Fenton's reagent; Solid waste

1. Introduction

Blast furnace flue dust is the waste dust of iron and steel industries, generally containing 20–50% of iron [1,2]. Till date, the iron and steel industry in China produces nearly 10 million tons of blast furnace flue dust every year. Most of the blast furnace flue dust is currently stockpiled on site, whereas small amounts of the dust are used in road aggregate fill material, soil stabilizers, and land amendments [3,4]. Because of the large quantities of material available and the consistent accumulation of the waste blast furnace flue dust, the utilization of the waste dust is an important research topic.

The coke wastewater mainly comes from coking, gas purification process, and refining process. It is a kind of industrial organic wastewater with wide source, large displacement, complicated composition, and toxicity. As a result, it is very difficult to be degraded [5,6]. The amount of phenolics is the highest among all the pollutants in the coke wastewater. Therefore, seeking an economic and efficient way to degrade the phenol in the coke wastewater is the key issue in the treatment of this kind of wastewater.

The major components of blast furnace flue dust are Fe_2O_3, FeO, ZnO, CaO, SiO_2, and MgO [7]. FeO and Fe_2O_3 can be dissolved to produce Fe^{2+} and Fe^{3+} in an acidic solution, and then Fe^{2+} and Fe^{3+} with hydrogen peroxide (H_2O_2) can form Fenton reaction system/Fenton-type reaction system [8–12]. As we all know, the hydroxyl radicals from Fenton reaction

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system are able to degrade organic chemicals, including phenol, efficiently.

The reaction mechanism is as follows [13]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \quad (1)$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^- \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (3)$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow O_2 + H_2O + {}^{\cdot}OH \quad (4)$$

$$ArOH + {}^{\cdot}OH \rightarrow \cdots \rightarrow CO_2 + H_2O \quad (5)$$

In this paper, the degradation of phenol and its oxidation intermediates are evaluated by blast furnace flue dust and H_2O_2 in acidic solution. Phenol was chosen as a typical organic component to simulate the pollutants in the wastewater. Factors including the pH of the solution, the initial H_2O_2 concentration, the amount of blast furnace flue dust, the reaction temperature, and the reaction time that affect the degradation rate of phenol were investigated in a batch of experiments. The degradation mechanism was also studied in detail by high-performance liquid chromatography (HPLC), X-ray diffraction (XRD), and ultraviolet–visible (UV–vis) spectrum.

2. Materials and methods

2.1. Materials

The following chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd: hydroquinone, pyrocatechol, maleic acid, and H_2O_2 (30%). Phenol was purchased from Tianjin Guangfu Fine Chemical Research Institute. The reagents used in this experiment are all of analytical grade.

The blast furnace flue dust samples used in this study were obtained from Wuhan Iron and Steel (Group) Corp. The major components of the fresh and spent blast furnace flue dust are listed in Table 1 (measured by flame atomic adsorption spectrophotometry).

2.2. Analysis

Phenol degradation rate was measured by 4-amino antipyrine direct photometric method at 510 nm. The results of the phenol treatment were characterized by a ultraviolet–visible spectrophotometer (Hitachi U3010). Phenol and its oxidation intermediates were determined by HPLC (Agilent 1100) with a mobile phase of 60% methanol/40% water with 0.25 mL/min at 275 nm. An diode-array detector was used in the experimental. The chemical oxygen demand (COD) value of the solution was determined following the classic potassium dichromate method [14].

2.3. General procedures

The blast furnace flue dust was sieved with a 120 mesh sieve and dried at 120℃ for 5 h in an oven. The degradation reaction was conducted in a 250 ml round-bottomed flask. A pH controller was used to control the pH of the solution by dropping 0.01 M NaOH or H_2SO_4 solution. The mixed liquor was stirred by a magnetic stirrer. After adjusting the initial pH of the solution to a desired value, H_2O_2 and the dried blast furnace flue dust were added into the reactor to start the degradation reaction. When the degradation is over, the remaining dust was separated as the spent dust. The phenol solution (1,000 mg/L) was used as the simulated wastewater in all the experiments.

3. Results and discussion

3.1. Study on the influence factors on the degradation rate

3.1.1. Effect of the pH value of the solution

Fe_2O_3 and FeO can be dissolved to produce Fe^{2+} and Fe^{3+} only by the acidic solution. Obviously, the reaction rate is greatly affected by the pH of the solution. Fig. 1 shows the effect of the pH value on the phenol degradation rate. When the pH is too low, it can inhibit the reaction of Eq. (3) and Fe^{3+} is difficult to be reduced to Fe^{2+}. As a result, the supply of Fe^{2+} of Eq. (1) is insufficient. Meanwhile, it is also not conducive to the production of ·OH. Consequently,

Table 1
The major components of the fresh and spent blast furnace flue dust

Weight (%)	TFe	Fe_2O_3	FeO	SiO_2	CaO	Al_2O_3	MgO
Fresh dust	66.28	30.71	32.23	18.84	9.86	2.96	1.85
Spent dust	20.10	11.23	5.26	49.02	23.58	5.33	1.12

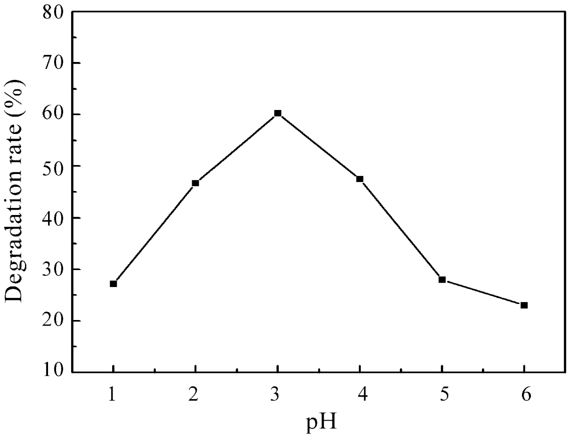

Fig. 1. The effect of the pH value of the solution on the degradation rate (conditions: 20 g/L blast furnace flue dust, 30 mmol/L H_2O_2, 35℃, and 2 h).

the degradation rate is low. When the pH is too high, it could inhibit the reaction of Eq. (1) and the generation of ·OH and Fe^{2+} and Fe^{3+} in the solution will be precipitated in a solution with high pH [15]. Therefore, the best pH in this case is 3.

3.1.2. Effect of the initial H_2O_2 concentration

Fig. 2 demonstrates the effect of the initial H_2O_2 concentration on the phenol degradation rate. It can be seen that the phenol degradation rate was increased with increase in the initial H_2O_2 concentration. The maximum degradation rate was obtained at the initial H_2O_2 concentration of 30 mmol/L. As the initial H_2O_2 concentration further increased, the degradation rate decreased because too many side reactions were initiated [16]. Thus, the optimal initial H_2O_2 concentration is 30 mmol/L.

3.1.3. Effect of the amount of blast furnace flue dust

Fig. 3 shows the effect of the amount of blast furnace flue dust on the phenol degradation rate. Increasing the amount of blast furnace flue dust will also increase the concentration of Fe^{2+}. As a result, more H_2O_2 was decomposed to form $OH^{\cdot}$ radical by Fe^{2+} catalysis. The concentration of $OH^{\cdot}$ radical is enhanced with the increase in Fe^{2+} concentration, and hence the phenol degradation rate increased. However, excess Fe^{2+} will consume the $OH^{\cdot}$ radical according to Eq. (2). Then phenol degradation rate decreased quickly due to the decrease in $OH^{\cdot}$ radical concentration [17]. Therefore, the best initial concentration of the blast furnace flue dust is 15 g/L. While in Figs. 1 and 2 the dust concentration of 20 g/L was selected to continuously provide Fe^{2+} and Fe^{3+} ions, then the Fenton's oxidation will sustain for longer time. Consequently, the effects of the pH value and initial H_2O_2 concentration on the phenol degradation rate can be investigated thoroughly.

3.1.4. Effect of the reaction temperature

Fig. 4 demonstrates the effect of temperature on the phenol degradation rate. It can be found that when the temperature is below 35℃, the phenol degradation rate increased with increase in temperature. However, when the reaction temperature was higher than 35℃, the phenol degradation rate was

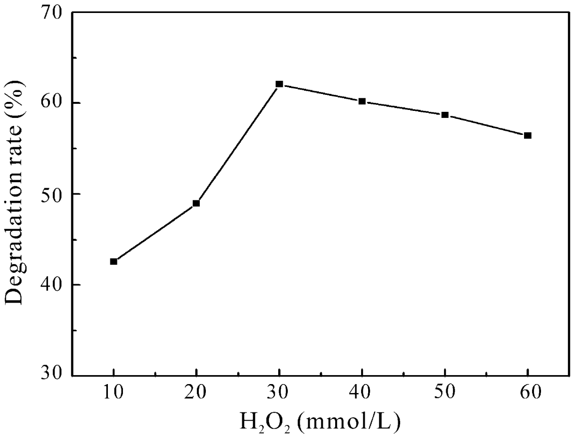

Fig. 2. The effect of the initial H_2O_2 concentration on the degradation rate (conditions: 20 g/L blast furnace flue dust, pH 3, 35℃, and 2 h).

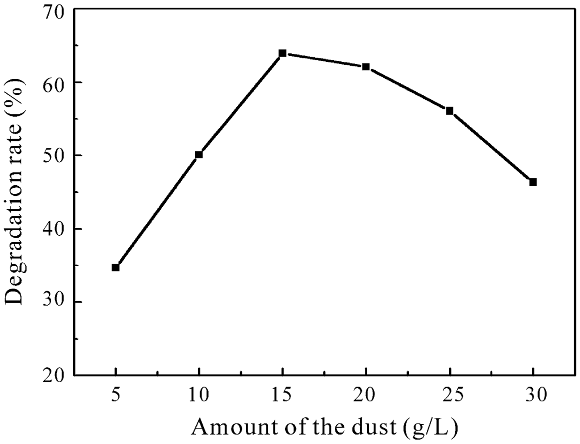

Fig. 3. The effect of the amount of blast furnace flue dust on the degradation rate (conditions: pH 3, 30 mmol/L H_2O_2, 25℃, and 2 h).

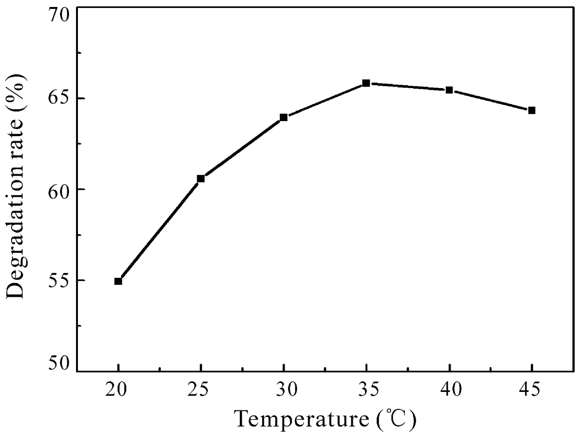

Fig. 4. The effect of the reaction temperature on the degradation rate (conditions: 15 g/L blast furnace flue dust, pH 3, 30 mmol/L H_2O_2, and 12 h).

decreased with temperature. This observation was consistent with other wastewater treatment processes [18]. As we all know, chemical reaction is accelerated by increase in temperature due to the increase of the average kinetic energy of the molecules. While in the Fenton reagent system, very high temperature will lead to decomposition of H_2O_2 to generate H_2O and O_2. Therefore, the suitable reaction temperature is 35℃.

3.1.5. *Effect of the reaction time*

The kinetics of the reaction using the blast furnace flue dust was also investigated in Fig. 5. It can be seen that the reaction was rapid until the reaction time is 12 h, at which the degradation rate was about 98%. Therefore, the optimal reaction time was selected to be 12 h under the current reaction conditions to degrade phenol completely. It is known that the Fenton reagent can oxidize many organic contaminants rapidly (within 30 min) [19,20]. The efficiency of the oxidation process is affected by the pH of the solution, temperature, H_2O_2 concentration, concentration of Fe^{2+}, and initial concentration of the contaminants. In this case, the blast furnace flue dust was used as the source of Fe^{2+} and Fe^{3+} ions. These ions were dissociated from the dust in the acidic solution. Therefore, comparing with the reaction time of other Fenton's reactions, this degradation process will sustain for longer time because of the continuous Fe^{2+} and Fe^{3+} ions being provided from the dust.

3.2. *Characterization results*

The UV–vis spectra of the simulated wastewater before degradation and the same solution after degradation under the optimal conditions (15 g/L blast furnace flue dust, pH 3, 30 mmol/L H_2O_2, 35℃, and 12 h) are shown in Fig. 6. A strong phenol characteristic absorption peak at 270 nm can be clearly observed in the spectrum of the simulated wastewater before degradation [21]. But the corresponding absorption peak of the solution after degradation disappeared, indicating that the phenol in solution has been degraded completely. The COD value of the simulated wastewater and the same solution after degradation was also examined by the classical potassium dichromate method. The test results indicated that the COD removal rate is 72% by this method.

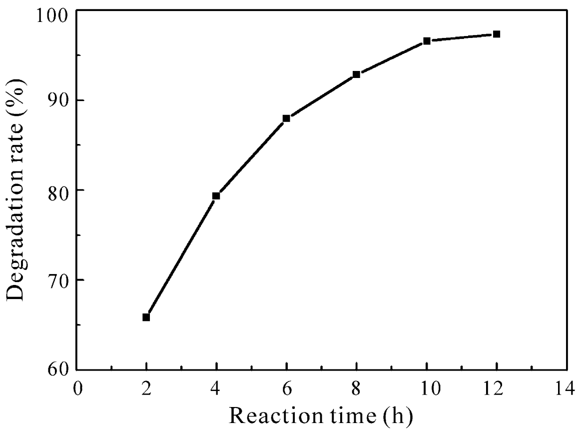

Fig. 5. The effect of the reaction time on the degradation rate (conditions: 15 g/L blast furnace flue dust, pH 3, 30 mmol/L H_2O_2, and 35℃).

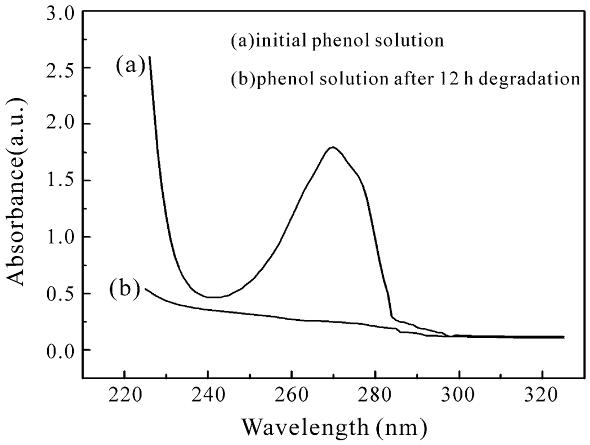

Fig. 6. The UV–vis spectrum of the solution of before and after degradation.

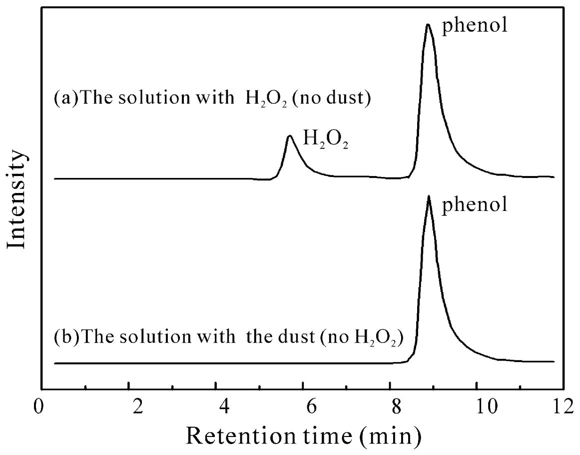

Fig. 7. The HPLC chromatograms of the reaction solution on different reaction conditions.

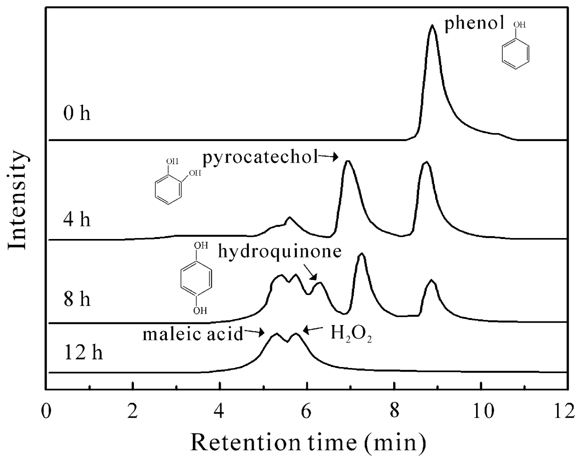

Fig. 9. The HPLC chromatograms of phenol degradation at different reaction time.

In fact, the HPLC chromatograms of the simulated wastewater with H_2O_2 (no blast furnace flue dust) and the simulated wastewater with blast furnace flue dust (no H_2O_2) were also carried out under the same degradation conditions (pH 3, 35℃, and 12 h). Fig. 7 shows that the intensity of the phenol peak was almost unchanged; therefore, we can infer that the degradation of phenol by Fenton system from the blast furnace flue dust and H_2O_2 did take place in the present case [22,23].

Fig. 8 illustrates the XRD patterns of the fresh blast furnace flue dust and spent dust. The diffraction peaks arising at 33.19˚, 35.73˚, 21.18˚, 39.30˚ and the peaks at 30.07˚, 43.06˚, 56.94˚, 62.53˚ in the fresh dust spectrum are corresponded to the crystalline nature of α-Fe_2O_3 and Fe_3O_4, respectively [24,25]. Compared with those of the fresh dust, the peak intensity of the spent dust decreased severely, which indicates that the iron species in the blast furnace flue dust have been dissolved in the acidic wastewater.

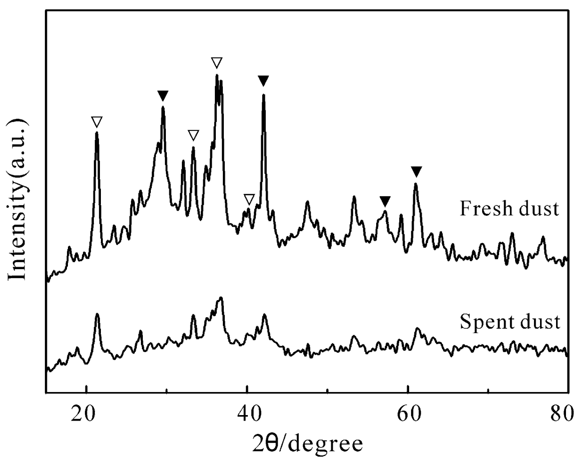

Fig. 8. XRD patterns of the fresh blast furnace flue dust and spent dust (▼ and ▽ denote peaks of α-Fe_2O_3 and Fe_3O_4, respectively).

3.3. *The mechanism analysis of degradation products by HPLC*

To reveal the degradation mechanism of the simulated wastewater by blast furnace flue dust and H_2O_2, the HPLC chromatograms of the simulated wastewater degradation for different time were also performed (Fig. 9). Based on our experimental results, the possible degradation pathway can be proposed as follows: phenol in the simulated wastewater was first oxidized into pyrocatechol and hydroquinone by the Fenton

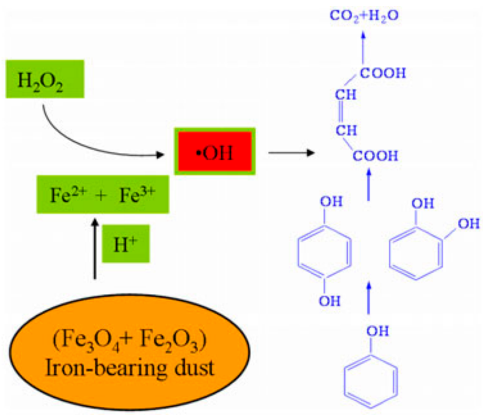

Fig. 10. The pathway of phenol degradation by the blast furnace flue dust and H_2O_2.

process, and then further oxidized into maleic acid, which was finally mineralized into CO_2 and H_2O (Fig. 10). Obviously, the blast furnace flue dust and H_2O_2 play a vital role in the degradation of phenol to CO_2 and H_2O [26,27].

4. Conclusions

In summary, a new treatment method to degrade phenol from simulated wastewater was studied using waste blast furnace flue dust with H_2O_2. The factors that affect the treatment efficiency were studied, including the pH of the solution, the initial H_2O_2 concentration, the amount of blast furnace flue dust, the reaction temperature, and the reaction time. The experimental results show that 1,000 mg/L of phenol in simulated wastewater is decomposed completely within 12 h by 15 g/L blast furnace flue dust with 30 mmol/L H_2O_2 in a solution whose pH was 3.0 at the temperature of 35℃. The mechanism of phenol degradation was also investigated by HPLC, XRD, and UV–vis spectrum in detail. Our study is hopeful to be developed as a novel method to degrade phenol from wastewater by waste blast furnace flue dust and H_2O_2.

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