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Research Article

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Heterogeneous Fenton Oxidation of H Acid in Water by Nanometer Zero-Valent Iron

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ABSTRACT

Nanometer zero-valent iron (NZVI) was prepared as the heterogeneous Fenton catalyst. The degradation of H-acid was investigated by heterogeneous Fenton-like oxidation. The influence of reaction time, amounts of H_2O_2, dosage of NZVI, solution pH and concentration of coexisting ions was investigated on degradation of H-acid by heterogeneous Fenton-like oxidation. The optimum conditions were obtained to be 60 min of reaction time, dosage of NZVI 0.03 g/L, solution pH of 3 and H_2O_2 amount of 80 mg/L for a H-acid concentration of 50 mg/L with a removal of 99.3%. The presence of sodium chloride and sodium sulfate hardly had a inhibition on H acid degradation.

Keywords: H acid; Nanometer zero valent-iron; Fenton-like oxidation; Degradation

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INTRODUCTION

H-acid (1-amino-8-naphthol-3, 6-disulfonic acid) is an important dye intermediate. It is widely used in chemical industry for the synthesis of direct, acidic, reactive and azoic dye, as well as in the pharmaceutical industry [1]. H acid wastewater always contains H acid, T acid (1-naphthylamine-3,6,8-trisulfonic acid), chromotropic acid (1,8-dihydroxy-3,6-naphthalene disulfonic acid), high concentration of inorganic salts and so on [2]. The H-acid manufacturing wastewater exhibits very high COD, acidity and chroma. H-acid wastewater may cause ecological and pose potential impact on drinking water quality if not be treated with proper and efficient methods before discharge [3]. Various methods have been used for the removal of H acid from wastewater such as chemical oxidation, extraction, membrane processes and adsorption [2-7]. Among advanced oxidation processes (AOPs), Fenton's reagent seems to be a promising process for decomposition of non-biodegradable and recalcitrant organic pollutants [8]. However, the traditional homogeneous Fenton process has many critical drawbacks, such as generated iron-containing sludge, neutralization of treated solutions before discharge, and even generates secondary pollution of acid or metal ions [9]. To overcome these disadvantages of the homogeneous Fenton process, the heterogeneous Fenton-like systems have been recently developed [10,11]. This study intends to prepare NZVI as the catalyst and use the Fenton-like oxidation for degradation H acid in aqueous solution.

EXPERIMENTAL SECTION

Chemicals and Reagents

The hydrogen peroxide solution (in mass % of 35) of analytical grade was obtained from Tianjin Fu Chen Chemical Reagent Factory. All aqueous solutions containing 50 mg/L H acid were prepared with distilled water obtained from a UP water purification system.

Preparation of NZVI

NZVI particles were synthesized by co-precipitation method. Briefly, 0.45 g of $FeCl_3 \cdot 6H_2O$ (0.45 g) were dissolved in 100 mL aqueous solution, then 60 mL of 1 M $NaBH_4$ solution was added dropwise into the $FeCl_3$ solution under stirring. After no gas generated at room temperature, the black nanoparticles were collected by rapid centrifugation, washed with deionized water to neutral pH, and then vacuum dried for use.

Catalytic Activity

In a typical catalysis test, a specified mass of NZVI particles was dispersed into 100 mL of H acid solution. The initial pH of solution was adjusted with diluted solutions of H_2SO_4 or NaOH. Degradation of H acid was initiated by adding H_2O_2. At selected time intervals, 0.5 mL samples were withdrawn and filtered immediately through 0.45 μm membrane filters to remove catalyst for analysis.

Analytical Methods

H acid concentration was measured by HPLC (Waters 2695) equipped with a Waters 2996 photodiode array detector, using a X Bridge Shield RP18 (150×4.6 mm, 3.5 μm) chromatographic column. The mobile phase was a mixture of 50% HPLC grade methanol and 50% ultrapure water (0.5% KH_2PO_4) for H acid, at a flow of 0.8 mL/min.

RESULTS AND DISCUSSION

Effect of H_2O_2 Concentration

The effect of H_2O_2 concentration between 20 and 120 mg/L on the H acid removal rate is depicted in Figure 1. Figure 1 showed that the removal efficiency of H acid after 40 min reaction were 67.3%, 74.4% and 70.1% when the concentration of H_2O_2 were 20, 80 and 120 mg/L in turn. As the concentration of H_2O_2 was increased from 20 and 80 mg/L, the removal efficiency of H acid was remarkably increased from 86.8% to 98.4% at 200 min. However, when the concentration of H_2O_2 was increased from 80 to 120 mg/L, the removal efficiency of H acid was decreased slightly. This might be caused by the increasing of H_2O_2 will produce more hydroxyl radicals and increase the oxidation ability. So removal efficiency of H acid also will increase. But, when the dosage of H_2O_2 is excessive, H_2O_2 would react with the hydroxyl radical [12]. It is a H_2O_2 self-consumption phenomenon. Besides the competition of the excessive H_2O_2 in the adsorption on the surface of catalyst, this limited the reactant concentration of H acid.

Effect of NZVI Dosage

Catalyst dosage is an important factor affecting the degradation of H acid. The effect of NZVI dosage on the removal efficiency of H acid is presented in Figure 2. As seen from Figure 2, when the dosage of NZVI was from 0.03 g/L to 0.07 g/L, the removal efficiency of H acid increased with the NZVI dosage increased. When the NZVI dosage was 0.03 g/L and 0.05 g/L, the removal efficiency of H acid can reach 99.31% and 99.37%, respectively.

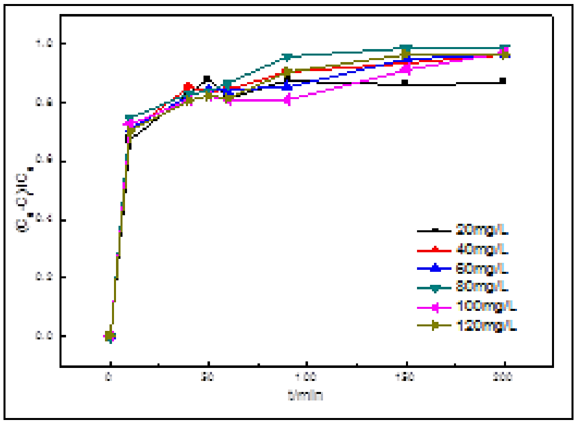

Figure 1: Effect of H_2O_2 concentration on the degradation of H acid

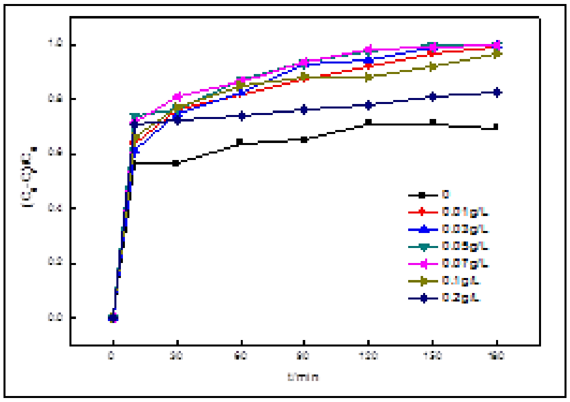

Figure 2: Effect of NZVI dosage on the degradation of H acid

Effect of Solution Initial pH

Solution initial pH of zero-valent iron activated hydrogen peroxide system has a greater impact, which greatly affects the removal efficiency of H acid. As seen from Figure 3, the removal efficiency of H acid reached the maximum value at pH 3 and 4. Decreasing the solution pH from 7 to 4 affected negatively the removal efficiency of H acid. The removal efficiency of H acid was enhanced from 48.7 to 99.3%. It was likely due to with the pH value of the solution increasing, the OH$^-$ concentration in the solution would increase. It may inhibit the formation of ·OH, and the number of ·OH that generated by the reaction would decrease. Therefore, the degradation of H acid was better under acidic conditions, and the pH is best at 3 and 4.

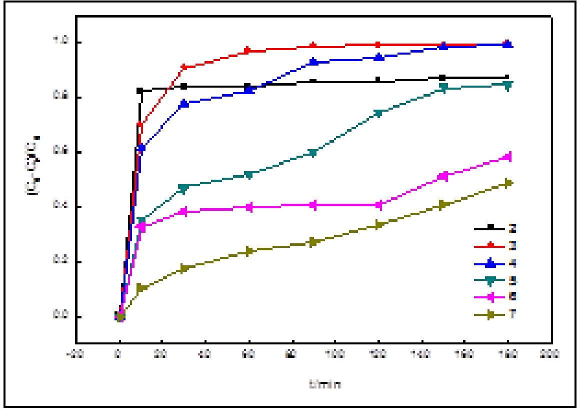

Figure 3: Effect of pH on the degradation of H acid

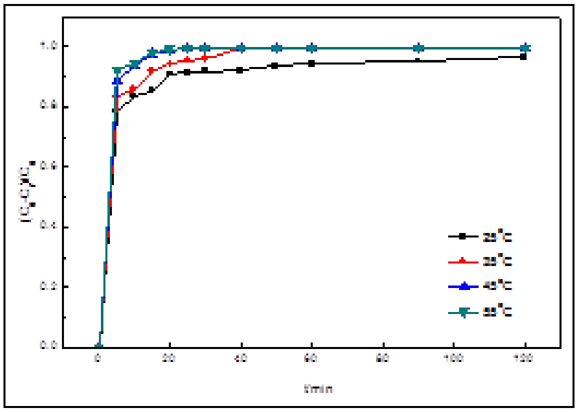

Figure 4: Effect of temperature on the degradation of H acid

Effect of Temperature

The effects of temperature on the H acid removal (Figure 4) were carried out at 25℃, 35℃, 45℃ and 55℃, respectively. During the experiments, pH of the solution did not change, it remained constant around 3. As shown in

Figure 4, H acid degradation was enhanced with the increase in temperature at at its initial stage, being 83.5, 85.7, 93.6 and 94.6% for temperatures of 25℃, 35℃, 45℃ and 55℃, respectively. This was expected due to the exponential dependency of the reaction rate constant on temperature. But, in the later stage, the removal efficiency of H acid was not enhanced with the increase in temperature (from 35℃ to and 55℃). For this reason, 35℃ seems to be a good temperature for heterogeneous Fenton-like oxidation of H acid by NZVI and H_2O_2 system.

Effects of Coexisting Ions

The removal efficiency of H acid in the treatment of wastewater is usually affected by the presence of various other coexisting anions. Therefore, the influence of different foreign ions (from 25 to 100 mg/L) towards the degradation of H acid (50 mg/L) has been investigated to determine the sensitivity of this method. Generally, wastewater contains more than one anion; common coexisting anions include SO_4^{2-} and Cl^-. Consequently, the presence of SO_4^{2-} and Cl^- may interfere with the removal efficiency of H acid. In this work, the effect of coexisting SO_4^{2-} and Cl^- on H acid removal by NZVI and H_2O_2 system was determined and showed in Figure 5. Figures 5a and 5b show the presence of SO_4^{2-} and Cl^- hardly interfered with H acid removal.

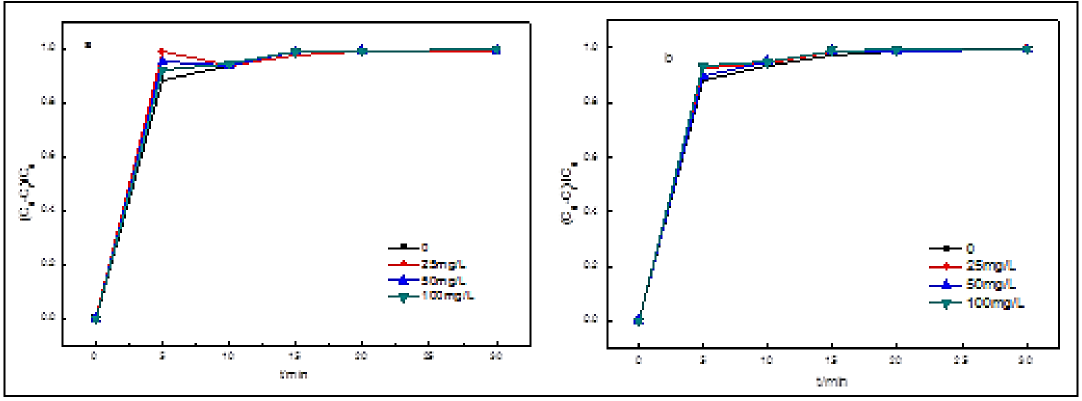

Figure 5: Effect of SO2- 4 (a) and Cl^-; (b) on the degradation of H acid

CONCLUSION

In this work, NZVI was prepared and Fenton-like oxidation was employed for the degradation of H acid in aqueous solution. The results showed that the optimum conditions were obtained to be 60 min of reaction time, solution pH of 3, NZVI dosage of 0.03 g/L and H_2O_2 amount of 80 mg/L for the H acid concentration of 50 mg/L with a removal efficiency of 99.3%. The presence of Cl^- and SO_4^{2-} does not obviously affect the degradation of H acid.

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