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The Treatment of Nanofiltration Concentrate of Coking Wastewater by Fenton Process

Jiao Wang

Hebei Energy College of Vocation and Technology, Tangshan, China

*wjiao82@126.com

Abstract. The nanofiltration concentrate of coking wastewater contain high concentration of nonbiodegradable and refractory organic matters. In this study, the nanofiltration concentrate was treated by Fenton process. The COD, NH_3-N and chrominance were selected as the target parameters. Their removal efficiencies were investigated through changing some operating parameters such as initial pH, initial H_2O_2 concentration, initial $FeSO_4$ concentration and reaction time. Under the optimum operating, the COD of effluent was below 85 mg / L, the removal rate was up to 85%; NH_3–N of effluent was reduced to 14 mg / L, the removal rate was up to about 94%; the removal rate of chroma reached about 85%,which satisfied the discharge water quality standards (chemical oxygen demand [COD] <100 mg/L, NH_3–N< 15 mg/L).In general, the fenton process can be a promising and reasonable method in the treatment of Nanofiltration concentrate of coking wastewater.

1. Introduction

Coking wastewater is produced in distillation of coal at high temperature and the deep processing of coal chemical products,which contains benzene, toluene, phenol, phenol, total cyanide, quinoline and polycyclic aromatic hydrocarbons and other hundreds of pollutants.It's a typical refractory organic wastewater of high concentration and toxicity[1.2]. With the development of membrane separation technology, nanofiltration has been widely used for removing COD, BOD, metal ions, bacteria, viruses, ammonia nitrogen from aqueous phase for high efficiency of separation, low operating pressure and pollution - resistant [3-6]. Specifically, ultrafiltration is selected in front of nanofiltration unit due to its effectively interception of macromolecules organic matter, colloid, suspended solids to ensure nanofiltration system maintain at a high throughput level X.W. Jin et al. [7] used ultrafiltration and nanofiltration combined for treating coking wastewater, and exhibited high removal effect. Ashaghi et al. used UF and NF ceramic membranes (membrane prepared from new materials) for the treatment of produced water.

However, the double membrane process is bound to produce a certain amount of nanofiltration concentrated solution. The analysis of water quality of the solution shows that the nanofiltration concentrate is a typical poor degradable organic chemical industrial with high salinity and total nitrogen. So advanced treatment techniques of nanofiltration concentrate are required.

Fenton oxidation is a efficient and advanced oxidation technology that produces a dual effect of chemical oxidation and flocculation. Fenton oxidation is composed of H_2O_2 and Fe^{2+}, producing hydroxyl radical (OH) with strong oxidizing ability (2.80 V) after the fluorine gas (2.87 V) in aqueous solution. Its reaction intermediate product can be combined with organic matter to generate organic free radicals, and ultimately organic matter is decomposed. So the COD in the wastewater is

greatly reduced or the refractory organic matter is decomposed into degradable organic matter. The Fenton process is composed of four successive stages, which are pH adjustment, oxidation, neutralization, and coagulation. The oxidation mechanism of the Fenton oxidation process is based on the generation of the reactive OH in the acidic condition by the catalytic decomposition of hydrogen peroxide [8].

Because of the production of nonselective OH, the organic compounds (RH) in wastewater are oxidized [9]. The study [10] also showed that the Fe^{3+} producted in reaction could react with OH^- to form Fe (OH) $_3$ precipitate, so Fenton reagent had flocculation function which was an important part of degradation of COD.

Compared with other advanced oxidation technologies (such as photocatalytic oxidation, ozone oxidation), Fenton oxidation has the advantages of simple operation process, easy to obtain, low running cost, simple equipment and friendly environment.

It has been reported that Fenton oxidation was used as pretreatment of waste water from ShaoGang coking plant, and the removal rate of heterocyclic organic compounds, benzene series, petroleum hydrocarbon, phenol and polycyclic aromatic hydrocarbons (PAHs) reached over 88%, and the removal rate of COD was more than 50.0%. H.Y. Xu et al [11] treated coking wastewater by fenton oxidation, the result showed the chrominance reduced from 1000 times to 50 times and COD removal rate reached more than 80%. L. Chu et al[12-15] used the Fenton reagent to treat the coking wastewater and reached the discharge standards.

The aim of the research was to investigate the effects of pH, H_2O_2 dosage, Fe^{2+} dosage and reaction time on the removal of COD, NH_3-N and chrominance in nanofiltration concentrate by Fenton oxidation. The optimum reaction conditions were determined and applied to industrial test.

2. Methods and Materials

2.1. Nanofiltration concentrate characteristics
Nanofiltration concentrate in this study was taken from a coke-oven plant in Tangshan, Hebei province, China. Its characteristics were shown in Table 1.

Table 1 Characteristics of Raw Wastewater

parameter	Average value
pH	8.5
COD (mg/L)	435
NH_3-N (mg/L)	168
Chrominance	368

2.2. Experimental system and procedure
This research was divided into two main stages. The first stage was in the laboratory. The 200mL of nanofiltration concentrate were added to the beaker, and the mixture was stirred by 200r/m. HCl was used to adjust to the required pH, and the temperature retained room temperature (25℃). $FeSO_4 \cdot 7H_2O$ solution and 30% H_2O_2 solution were added in the required amount, and mixed the stirrer to the desired time. The reaction mixture was allowed to stand for a period of time and the supernatant was used for analysis. Single factor optimization test was carried out when one of the factors such as H_2O_2 dosage, Fe^{2+} dosage, initial pH, reaction time were changed.
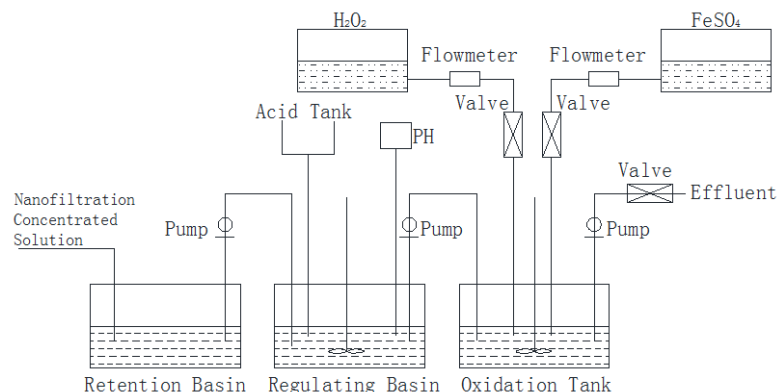
Figure 1. Diagram of industrial test installation

The second stage was the industrial test. The industrial test was carried out in two Fenton reaction tanks with a volume of 100 m^3 and treatment capacity of 125m^3 / d（Figure 1）. The pH was adjusted by adding HCl to the fenton oxidation tank, and fenton oxidation was carried out by adding 30% H_2O_2 and $FeSO_4$ according to the COD concentration of raw wastewater. Blew to the oxidation tanks to ensure that the reagent and concentrated solution in full contact during the whole process.The aeration was stopped after 1h reaction,and then the results were sampled.

2.3. Analytical methods
Solution pH was monitored by glass electrode method (GB / T 6920). All theanalyses were carried out in accordance with the Standard Methods of the APHA (APHA, 1995). COD was determined utilizing dichromate method (GB11914-89) . TN was measured according to the infrared spectrophotometry (GB / T 16488-1996).

3. Result and Discussion

3.1. Effect of Fe^{2+} initial concentration on removal efficiency
The effect of Fe^{2+} dosage on the oxidation of Fenton reagent was investigated under the conditions of reaction temperature of 25 °C, initial pH of 4, dosage of H_2O_2 of 400 mg / L and reaction time of 60 mins.The result was shown in Figure 2.
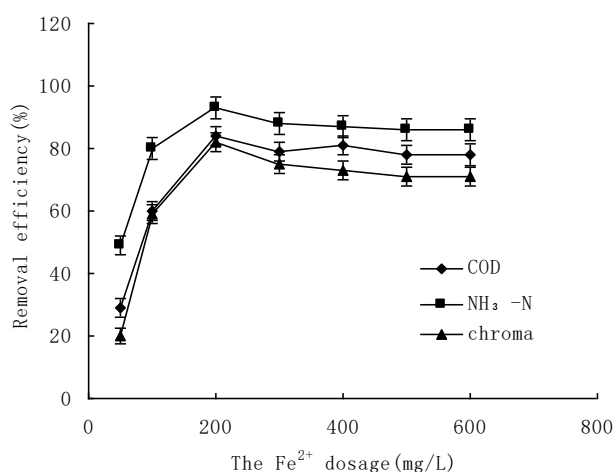

Figure 2. Effect of Fe^{2+} dosage on COD, NH_3-N and chroma removal efficiency in Fenton progress

As shown in Figure 2, when concentration of Fe^{2+} was low, the addition of Fe^{2+} would enhance COD, NH_3-N and chrominance removal. 84% COD was removed when the concentration of Fe^{2+}

dosage was 200 mg/L. but when the dosage of Fe^{2+} increased to a certain extent, COD, NH_3-N and chrominance removal rates were no longer increased, instead of decreased. It's because Fe^{2+} mainly acted as a catalyst in Fenton oxidation. With the increase of catalyst concentration, the quantity of ·OH increased, COD, NH_3-N and chrominance removal rates improved obviously. However, when the concentration of Fe^{2+} was too high, due to its strong catalytic effect, H_2O_2 produced a large number of OH rapidly. Some OH which had no time to oxidize the organic matter in the wastewater reacted with each other to produce H_2O and O_2. Part of the initial production of OH was consumed causing that COD, NH_3-N and chrominance removal rates declined.

There was another reason that excess Fe^{2+} had reacted with ·OH resulting in a decrease in COD, NH_3-N and chrominance removal rates. In addition, a large number of Fe^{2+} addition would increase the difficulty of subsequent treatment of wastewater. Therefore, the best dosage of Fe^{2+} was 200 mg / L.

3.2. Effect of H_2O_2 initial concentration on removal efficiency
To investigate the effect of H_2O_2 dosage during the direct Fenton process, a series of experiments were conducted at different concentrations of H_2O_2, ranging from 200 to 800 mg/L, and reaction temperature of 25 °C, initial pH of 4, dosage of Fe^{2+} of 200 mg / L and reaction time of 60 mins.

The results are shown in Figure 3. COD, NH_3-N and chrominance removal rates increased with the increase of H_2O_2 dosage, however, when the dosage of H_2O_2 increased to a certain extent, COD, NH_3-N and chrominance removal rates decreased with the increase of H_2O_2 dosage. It's because the H_2O_2 dosage would increase the generation of OH so that COD, NH_3-N and chrominance removal rates increased rapidly. When H_2O_2 was added in excess, the higher concentration of H_2O_2 not only exacerbated its own decomposition reaction, but also consumed OH by itself.

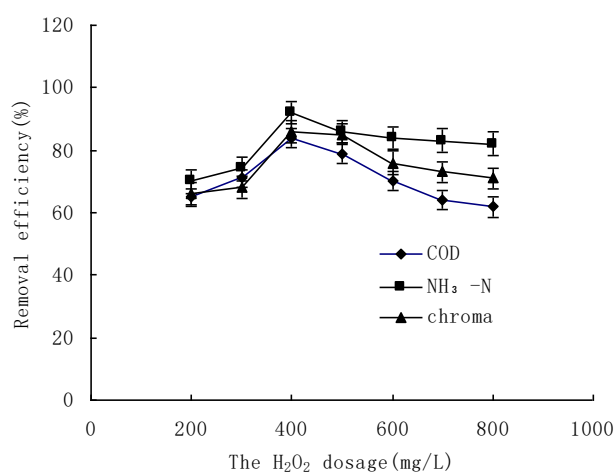**Figure 3.** Effect of H_2O_2 dosage on COD, NH_3-N and chroma removal efficiency in Fenton progress

In addition, Fe^{2+} was oxidized to Fe^{3+} by the excessive amount of H_2O_2, leading to a large number of OH consumed in Fe^{2+} catalytic oxidation process, meanwhile chrominance of wastewater rose because of slightly soluble Fe^{3+}. Studies [16] shown that the residual H_2O_2 in wastewater would exhibit reduced activity to consume potassium dichromate.From the effect and the cost, the appropriate dosage of H_2O_2 was 400mg / L .

3.3. Effect of initial pH on removal efficiency
The effect of initial pH on removal efficiency was investigated under the conditions of reaction temperature of 25 °C, dosage of Fe^{2+} of 200 mg / L, dosage of H_2O_2 of 400 mg / L and reaction time of 60 mins. The result was shown in Figure 4.
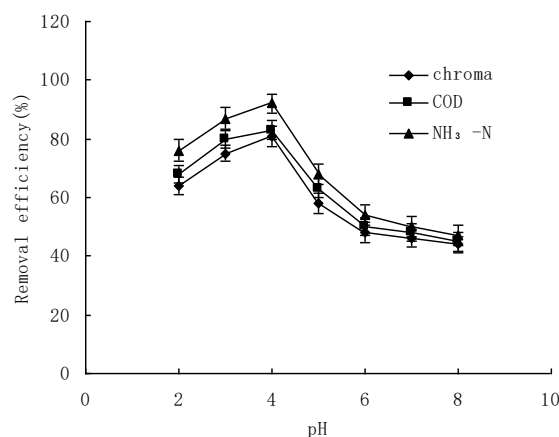
Figure 4. Effect of initial pH on COD, NH_3-N and chroma removal efficiency in Fenton progress

The results showed that when the initial pH of raw water increased from 2 to 8, the removal rate of COD increased at first then decreased. The removal efficiency of COD was the best at the pH of 4.

3.4. Effect of operrating time on removal efficiency

To investigate the effect of reaction time during the direct fenton process, a series of experiments were conducted at different reaction time, ranging from 20 to 140mins, and reaction temperature of 25 °C, initial pH of 4, dosage of Fe^{2+} of 200 mg / L and dosage of H_2O_2 of 400 mg / L.
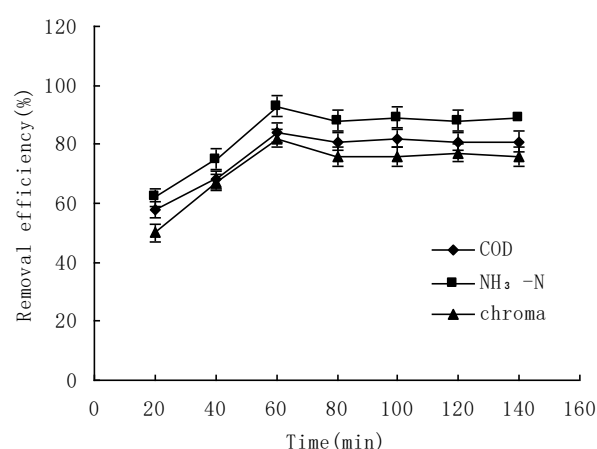

Figure 5. Effect of reaction time on COD, NH_3-N and chroma removal efficiency in Fenton progress

It's shown in Figure 5 that Fenton oxidation of organic reactions mainly occurred in the first 60 mins, The initial reaction rate of Fenton oxidation was faster, and the removal rate of COD was 81% at first 60 mins. When the reaction time was more than 60 mins, the removal rate of COD reached 82%, and the change was not obvious. It's because the H_2O_2 of the fenton reagent had been consumed after 60 mins, no longer produced OH to react with organic. Due to the increase of coagulation, the removal rate of COD was slightly increased after 60 mins. However, the infrastructure and operating costs would increased as the reaction time prolonging in the actual project. So the best reaction time for this study was 60 mins.

3.5. Industrial test

According to the pH of the nanofiltration concentrate, the pH was adjusted to about 4.0 in the process to the Fenton oxidation tank, and fenton oxidation was carried out with adding 400mg / L H_2O_2 and

200mg / L FeSO$_4$.The effect of stable operation in 10 frequencies was shown in Figure 6 .
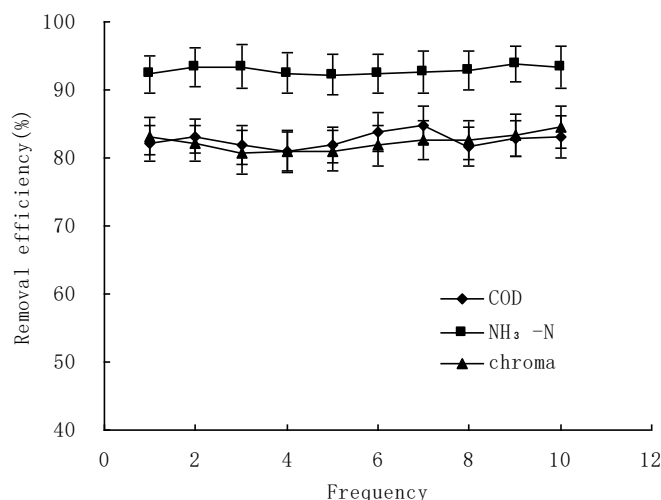

Figure 6. Removal efficiency of industrial test

It was seen from the Figure 6. that the removal efficiencies of COD, NH$_3$-N and chrominance were relatively stable, and the COD of effluent was below 85 mg / L, the removal rate was up to 85%; the NH$_3$-N of effluent reduced to 14 mg / L, the removal rate was up to about 94%; The removal rate of chroma reached about 85%.

4. Conclusion

Experimental results showed that the treatment efficiency of nanofiltration concentrate of coking wastewater using Fenton process was affected by the dosage of H$_2$O$_2$ and Fe^{2+}, initial pH and reaction time. At an influent COD concentration of 260mg/L, the optimum reaction conditions were: 333mg/L of H$_2$O$_2$, 200mg/L of Fe^{2+}, initial pH of 3 and 60 min of reaction time.

Under the above optimum reaction conditions, an industrial test was carried out. The COD concentration, NH$_3$-N concentration and color were reduced to 65mg/L, 11mg/L and 56PCU respectively, and their corresponding removal rates reach 85%, 94% and 85%. Fenton is one of the advanced oxidation processes that can steadily treat nanofiltration concentrate of coking wastewater to grade one standard of "Integrated Wastewater Discharge Standard" (GB 8978-1996), and is expected to enable the recycling of wastewater within the plant.

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