



Removal of cyanide compounds from coking wastewater by ferrous sulfate: Improvement of biodegradability



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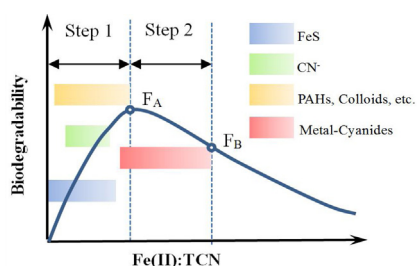
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HIGHLIGHTS

- Reaction between ferrous and coking wastewater was a two-step process.
- Mechanisms of the first step included FeS precipitation, CN⁻ complex and organics coagulation.
- Mechanism of the second step was dominated by the immobilization of metal–cyanide compounds.
- The biodegradability of coking wastewater was achieved at the end of the first-step process.
- The optimal ferrous dosage should be determined by the characteristics of coking wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of ferrous sulfate (FeSO_4) treatment on the removal of cyanide compounds and the improvement of biodegradability of coking wastewater were investigated by varying Fe:TCN molar ratios. Results suggested that the reaction between FeSO_4 and coking wastewater was a two-step process. At the first step, i.e., $0 \leq \text{Fe:TCN} \leq 1.0$, the reaction mechanisms were dominated by the precipitation of FeS, the complexation of CN⁻, and the coagulation of organic compounds. The COD of coking wastewater decreased from 3748.1 mg/L to 3450.2 mg/L, but BOD₅:COD (B/C) was improved from 0.30 to 0.51. At the second step, i.e., $1.0 < \text{Fe:TCN} \leq 3.2$, the immobilization of soluble metal–cyanide compounds by ferrous ions was the dominating mechanism. The COD showed a continuous increase to 3542.2 mg/L (Fe:TCN = 3.2) due to the accumulated ferrous ions in coking wastewater. Moreover, B/C decreased progressively to 0.35, which was attributed to the negative effects of excess ferrous ions on biodegradability. To improve coking wastewater's biodegradability, a minimum ferrous dosage is required to complete the first step reaction. However, the optimum ferrous dosage should be determined to control a safe residual TCN in coking wastewater for the further biological treatment.

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1. Introduction

Coking wastewater is a typical industrial organic wastewater, which is characterized as high organic load, complicated composition and strong toxic/inhibitory [21,24]. China, as the largest coke-producing country, is currently facing huge challenges in dealing with the pollution of coking wastewater [17,25]. Coking wastewater was commonly reported with an extremely low biodegradability (e.g., $BOD_5:COD < 0.3$) [23]. The traditional industrial wastewater treatment, i.e., physicochemical pretreatment followed by biological oxidation/digestion, encountered a series of difficulties, e.g., long hydraulic retention time (HRT), difficult sludge acclimation, weak resistance to impact load and high construction cost, for eliminating the hazardous compounds. Cyanide is a characteristic contaminant of coking wastewater, being a major toxic component inhibiting biological process. According to Kim et al. [10], free cyanide (CN^-) above 0.2 mg/L will cause serious inhibition of nitrification of coking wastewater. Therefore, effective preliminary elimination of cyanide compounds has become a basic requirement for the biological treatment.

Ferrous and ferric salts are the common reagents used in removing cyanide compounds from industrial wastewater such as mining wastewater [1], metallurgical wastewater [18], and coking wastewater [14,16]. The major removal mechanism is the complex reaction with cyanide compounds to form precipitates such as Prussian blue ($Fe_4[Fe(CN)_6]_3$) and Turnbull's Blue ($Fe_3[Fe(CN)_6]_2$) [6]. Park et al. [14] studied the treatment of cyanide-containing effluent with ferrous and ferric salts, suggesting that both chemicals were able to remove the total cyanides (TCN) efficiently. Ryu et al. [16] studied the effect of ferrous coagulation on the biological nitrification of coking wastewater, showing that ferrous coagulation contributed about 35% enhancement of NH_4^+ removal compared to that of non-coagulated coking wastewater due to the preliminary removal of CN^- .

Despite multiple studies of successful application, the specific reaction mechanism between ferrous ions and coking wastewater is still uncertain due to the complicated composition of coking wastewater. For example, there are some other contaminants also able to react with ferrous ions, such as sulfide (S^{2-} , through precipitation) and colloids (through coagulation of Fe^{2+} hydrolysis). These substances compete with cyanide compounds for ferrous ions. Hence, all these factors should be considered in determining the optimum dosage of ferrous ions. To the best of our knowledge, there is no published paper discussing the detailed mechanism of this competitive process. As a result, the determination of the ferrous dosage in practical treatment remains relying mostly on practical experience, and there is no general guideline for the predictive calculation.

In this work, the reaction mechanism between ferrous sulfide and coking wastewater was investigated by varying ferrous dosages. The objective of this study is to explore the relationship between ferrous dosage and coking wastewater's biodegradability. Multiple parameters were examined to analyze the competitive mechanism between cyanide compounds and other contaminants. The effect of ferrous dosage on the biodegradability of coking wastewater was evaluated by BOD_5 and $BOD_5:COD$ (B/C). Further-

more, a general method for calculating the optimum ferrous dosage in pre-treating coking wastewater was proposed.

2. Materials and methods

2.1. Coking wastewater

Coking wastewater used in this study was collected from the wastewater treatment plant (WWTP) of Shaoguan Steel Company, located in Guangdong, province of China. The company's affiliated coking plant has a coke production capability of 1.32 million metric tons per year and generates about 2000 m³ coking wastewater per day. The biological treatment of WWTP was designed as a sequential anoxic-oxic-hydrolytic-oxic (A/O/H/O) system. Physicochemical pretreatments (i.e., air-floatation for oil removal, ferrous precipitation for cyanide and sulfide removal) and post-treatment (i.e., coagulation for suspended microbial products) were also employed for enhancing treatment effect. 10 L of raw coking wastewater were collected from the intake of WWTP using acid-washed, glass bottles that were pre-rinsed with the sample wastewater. The wastewater samples were kept on ice during transportation from WWTP to the laboratory. Table 1 shows the main characteristics of coking wastewater monitored by WWTP and for the sample used in this work.

2.2. Treatment with ferrous sulfate

Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Sigma–Aldrich) was used to remove cyanide compounds from raw coking wastewater. A series of $FeSO_4 \cdot 7H_2O$ dosages were determined according to the $Fe(II):TCN$ molar ratio at 0.00, 0.15, 0.50, 0.65, 0.80, 1.00, 1.20, 1.60, 2.00, 2.40 and 3.20. The jar test was conducted by the six-paddle stirrers (0–300 rpm, Hanuo Co., Ltd., China) to investigate the effect of ferrous dosage. The jar test included three steps: rapid agitation, slow agitation and settling. Firstly, the 200.0 mL coking wastewater sample was placed to a 250 mL beaker, to which a preset amount of $FeSO_4 \cdot 7H_2O$ was added and the sample was stirred rapidly at 200 rpm for 5 min. Subsequent to the rapid mixing, the sample was slowly agitated at 50 rpm for 10 min. Finally, the agitation stopped and the sample was allowed to settle for 30 min. The supernatant was filtered through a 0.45 μm filter prior to be analyzed for free cyanide (CN^-), total cyanide (TCN), total organic carbon (TOC), total inorganic carbon (TIC), COD, BOD_5 and pH.

2.3. Analytical methods

The determinations of CN^- and TCN were carried out following the reference method [12]. TOC concentration was measured by a TOC-VCPH carbon analyzer (Shimadzu, Japan). COD and BOD_5 were measured according to standard methods (APHA, 2005). COD was measured by the closed reflux colorimetric method. Dilution water used for BOD_5 measurement was seeded with the extraction of aerobic sludge from WWTP. The HACH BODTrak II manometric respirometer (USA) was employed to determine the oxygen level of samples at $21 \pm 0.5^\circ C$. The concentration of H^+ ions in the treated coking wastewater was calculated from the pH values.

Table 1
Basic characteristics of coking wastewater tested for ferrous treatment.

	COD ($mg L^{-1}$)	TOC ($mg L^{-1}$)	BOD_5 ($mg L^{-1}$)	TCN ($mg L^{-1}$)	S^{2-} ($mg L^{-1}$)	NH_4^+-N ($mg L^{-1}$)	CN^- ($mg L^{-1}$)	pH	Chromaticity
1 ^a	3500 ± 600	1050 ± 150	850 ± 250	46 ± 10	47 ± 25	281 ± 100	3.5 ± 2.1	9 ± 2	120 ± 40
2 ^b	3748.1	1175.6	1098.7	53.6	49	195.3	3.2	9.12	128

^a Average monitoring values of WWTP.

^b Coking wastewater used in this study.

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