Original Research

Influential Factors on Activated Sludge Deterioration in Anoxic-Oxic (A/O) Biological Treatment of Coking Wastewater

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Abstract

The control measures for deterioration of aerobic activated sludge were experimented. Wastewater samples with different pH, temperature, SVI, and MLSS were investigated to detect the cause of sludge deterioration. The results show that after being operated at high $S_2O_3^{2-}$ (which could lead to a pH decrease) loading in an A/O biological reactor treated for coking wastewater, though the pH was controlled at about 7.0 by the addition of NaOH, the COD removal efficiency was decreased deeply. The MLSS decreased from 3,800-4,300 mg/L to 2,020 mg/L after loading of $S_2O_3^{2-}$ and NaOH in the oxic unit of A/O biological reactor for 12 days. The COD removal efficiencies and MLSS concentrations were decreased sharply when the wastewater's temperature was over 30ºC, which indicates the bulking of activated sludge in the oxic unit of A/O biological reactor. The results suggest that it cannot inhibit the occurrence of sludge deterioration only by controlling the pH in the oxic unit of an A/O biological reactor. Although the addition of NaOH could inhibit sludge bulking, the decreased MLSS concentration would significantly reduce the COD removal efficiency. The decline of COD removal efficiency may be due to the high temperature leading to sludge death.

Keywords: activated sludge, coking wastewater, anoxic-oxic (A/O) biological treatment, sludge deterioration, acidification

Introduction

Coking wastewater, which is produced from quenching of hot coke and washing the produced gas in coking plants, contains high concentrations of ammonia, phenols, thiocyanate, cyanide, and lower amounts of other toxic compounds [1, 2]. According to the coal quality and the properties of the coking process, the individual concentration of the contaminants is different. Coking wastewater treatment usually consists of both physico-chemical and biological units. Recently, some new methods have been applied to the coking wastewater treatment. Various techniques, including electrochemical oxidation [3], ultrasonic/ozone combined methods [4], biofilm reactors combined with zero-valent iron process [5], filtration and adsorption using manganese and magnesium ores [6], and electro-Fenton oxidation, have been investigated to remove pollutants from coking wastewater [7]. However, due to the construction investment and operating costs, it is no doubt that the biological method is the mainstream approach in the treatment of coking wastewater. Generally, the mainly biological treatment method for coking wastewater is anoxic-aerobic (A/O) processing [8].

Occasionally, in practical applications, the A/O biological treatment is not stable. On the basis of survey data of the Tangshan Kailuan coking plant, it found that the activated sludge of the A/O biological system has occasionally functioned abnormally, which led to the high concentration of

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effluent. It usually took the activated sludge system 10-60 days to return to its normal performance, thus causing a severe problem for effluent to meet the discharge standard of coking wastewater.

Until now, few studies have analyzed the influential factors on activated sludge deterioration in A/O biological treatment of coking wastewater. Chao et al. reported that pH decrease, caused by the increase of $S_2O_3^{2-}$ concentration, was apparently a key factor causing sludge deterioration (acidification) [9]. Martins A M P et al. considered that DO concentration, different influent feeding pattern, and storage on sludge settling ability had an effect on sludge deterioration [10, 11]. Felfoldi et al. found that some genus *Thiobacillus* and identified bacteria (e.g. *C. badia* and the *Ottowia*-related strains) had a significant impact on the structure of the activated sludge and deterioration [1].

Thus, it is necessary to identify the most relevant cause of sludge deterioration and find a feasible resolution to the referring problem. Accordingly, in this study, the control measures for deterioration of aerobic activated sludge were experimented. A 40.5L model A/O biological treatment reactor was set up to simulate the real wastewater treatment system. The wastewater sample with different pH, temperature, SVI, and MLSS was investigated to detect the cause of sludge deterioration.

Materials and Methods

Characteristics of the Wastewater and Activated Sludge

The wastewater sample used for the experiment is the real coking wastewater collected from Tangshan Kailuan coking plant. Typical composition of the coking wastewater is shown in Table 1.

Activated sludge-mixed liquor taken from the Tangshan Kailuan coking plant was used as the seed for this experiment. Nutrients (KH_2PO_4, K_2HPO_4, $Na_2HPO_4 \cdot 7H_2O$, NH_4Cl, $MgSO_4$, $CaCl_2$, and $FeCl_3$) with different concentration were added into the reactor at the initial stage of acclimation. After about 20 days, when the removal efficiencies of COD and NH_4^+-N were relatively stable, the sludge cultivation was finally completed.

Experimental Setup

The main body of A/O biological treatment model reactor consisted of an anoxic unit (300×200×300 mm) and an oxic unit (300×250×300 mm). A coking wastewater sample was pumped into the anoxic unit, where the acidification degradation occurred with the action of acidogenic bacteria. The effluent from the anoxic unit overflowed to the oxic unit, where aeration occurred.

Materials

All chemicals used in the experiments were reagent grade or higher and were used as received without further purification. Hydrochloric acid (HCl), sulphuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), NaOH, $NaHCO_3$, anhydrous sodium carbonate, and mercury sulfate were obtained from Beijing Chemical Co., Ltd. Ammonium molybdate, sodium thiosulfate, sodium bicarbonate, magnesium sulfate, calcium chloride, and silver sulfate were supplied by Tianjin Jinke Fine Chemicals Institute. Manganese sulfate, potassium iodide, aluminum potassium sulfate, urea, potassium dihydrogen phosphate, glucose, starch, and other nutrients were purchased from Xilong Chemical Engineering Co., Ltd.

Table 1 Characteristics of coking wastewater from Tangshan Kailuan coking plant.

Parameter	Characteristics
pH	7.5-9.0
Temperature (ºC)	20-40
COD (mg/L)	1500-2200
Phenols (mg/L)	300-450
CN^- (mg/L)	5-20
NH_4^+-N (mg/L)	400-900

Analytical Methods

The concentrations of different contaminant in the wastewater were analyzed for various parameters according to standard methods of China [12]. COD was determined using the potassium dichromate titration method. Ammonia nitrogen test was performed using colorimetry method, and pH value was measured by a Shanghai Leici PHS-3D brand pH-meter. MLSS and SVI were determined by gravimetric method.

Results and Discussion

Effect of pH Value

Chao et al considered that overloading of $S_2O_3^{2-}$ in coking wastewater was apparently a key factor causing sludge acidification and the pH control in the aerobic biological treatment stage can inhibit the sludge deterioration [9]. Williams and Unz confirmed through experiments that the sludge deterioration of aerobic biological treatment unit was related with organic acid concentration [13]. In this study, the experiments were tested to verify whether it could cause the sludge deterioration with loading of $S_2O_3^{2-}$ and whether it could restrain the sludge deterioration with adjustment single factor of pH in coking wastewater. The process was as follows: coking wastewater loaded with 1,000 mg/L $S_2O_3^{2-}$ was fed into A/O model-activated sludge reactors. The pH in the oxic unit was controlled at about 7.0 by automatic NaOH titration. The COD concentrations in influent and effluent of the oxic unit were monitored with respect to time. The results are shown in Fig. 1.

As shown in Fig. 1, the degradation of COD was kept stable at about 80%. After the addition of 1,000 mg/L $S_2O_3^{2-}$ on the third day of operation, the influent COD increased from 1,845 mg/L to 1,860 mg/L. The pH of wastewater was continuously monitored and always controlled at about 7.0 by the addition of NaOH when pH was dropped. After being operated at high $S_2O_3^{2-}$ loading for 10 days, COD removal efficiency was not changed much. In contrast, after 13 days of operation, the COD removal efficiency was decreased sharply until at its lowest of below 20%. This indicates that it cannot inhibit the occurrence of sludge deterioration only by controlling the pH in the oxic unit of the A/O biological reactor, which is different with the research conclusions of Chao [9].

Effect of SVI and MLSS

The MLSS and SVI values of activated sludge in oxic unit of A/O biological reactor were determined also, which was shown in Fig. 2.

Fig. 2 shows that SVI values remained below at 200 ml/g within 20 days operation time, which illustrated that there was no sludge bulking in the oxic unit of the A/O biological reactor. At the initial 9 days of operation, the MLSS values were generally between 3,800-4,300 mg/L. However, after loading of $S_2O_3^{2-}$ and NaOH in the oxic unit for 12 days, the MLSS values sharply decreased to 2,020 mg/L. These results suggest that although the addition of NaOH could inhibit sludge bulking, the decreased MLSS concentration would significantly reduce COD removal efficiency.

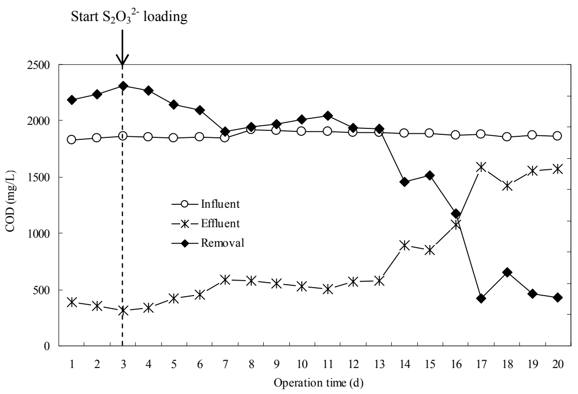

Fig. 1. COD composition in the influent and effluent of an $S_2O_3^{2-}$-loaded A/O activated sludge reactor.

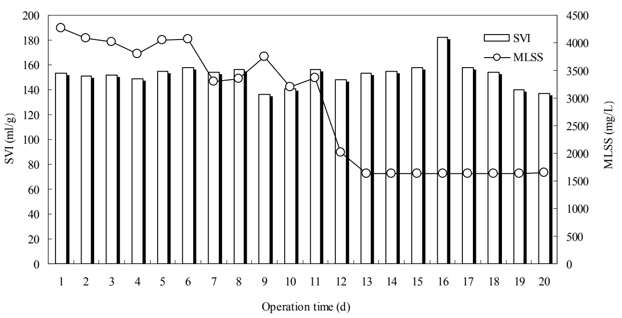

Fig. 2. The MLSS and SVI values of activated sludge in the oxic unit of an A/O reactor.

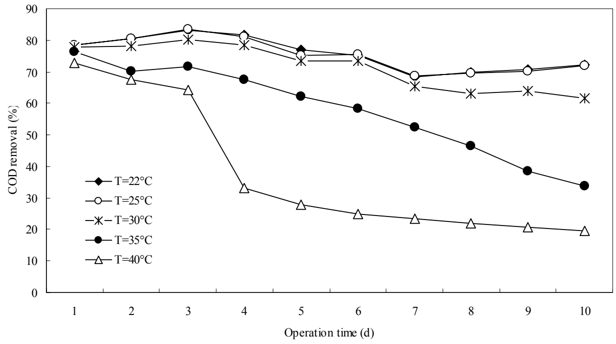

Fig. 3. COD removal efficiency with different temperatures in the oxic unit of an A/O biological reactor.

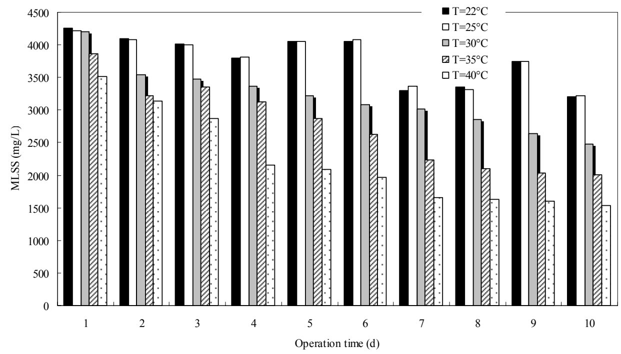

Fig. 4. MLSS with different temperatures in the oxic unit of an A/O biological reactor.

Effect of Temperature

Another possible mechanism of sludge deterioration is wastewater temperature. The temperature in the oxic unit was controlled from 22ºC to 40ºC by electric heater. The COD removal efficiency and MLSS of oxic unit was monitored with respect to time. The results are shown in Figs. 3 and 4.

As shown in Figs. 3 and 4, the COD removal efficiencies and MLSS concentrations were decreased sharply when the wastewater's temperature was over 30ºC, which indicates the bulking of activated sludge in the oxic unit of an A/O biological reactor. The decline of COD removal efficiency may be due to the high temperature leading to sludge death. However, in real coking wastewater treatment plants the temperature of wastewater is usually in the range of 30-40ºC. It is necessary to reduce the temperature of wastewater in the A/O biological treatment of coking wastewater below 30ºC.

Based on previous literature [9], Chao et al. found that $S_2O_3^{2-}$ concentration was most likely the reason for sludge acidification, which caused sludge deterioration in activated sludge reactor of coking wastewater treatment. And controlling the pH of activated sludge reactor at 6.0-7.0 was effective in avoiding this effect and in maintaining the biodegradation function. In this work, pH, temperature, SVI, and MLSS of sludge was investigated to identify the most relevant causes for sludge deterioration and the feasible controlling suggestion was proposed (rather than simply relying on pH value).

Conclusions

The study shows that after loading $S_2O_3^{2-}$ into an A/O biological reactor treated for coking wastewater, the control of pH at neutral could not inhibit the COD removal efficiency decrease. Although the addition of NaOH could inhibit sludge bulking, the decreased MLSS concentration would significantly reduce COD removal efficiency. The COD removal efficiencies and MLSS concentrations were decreased sharply when the wastewater's temperature was in the range 30-40ºC. It is necessary to reduce the temperature of wastewater in the A/O biological treatment of coking wastewater below 30ºC.

Acknowledgements

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