Treatment of Cleaning Wastewater from the Desulfurization Slag Recycling Plant

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It was found that the chemical oxygen demand (COD) of the wastewater from the desulfurization slag recycling plant occasionally exceeded the set value. Two of the most common oxidants, H_2O_2 and NaOCl were employed to reduce COD. The optimal dosage of H_2O_2 (30%) and NaOCl (10%) were 0.4% and 8.0% (volume ratio) of the wastewater, and the residual COD were 155 and 123 mg/L, respectively. The elimination capacity of H_2O_2 and NaOCl ranged from 0.42 - 0.47 and 0.15-0.22 g $\triangle$COD/g oxidant. The specific cost of H_2O_2 and NaOCl ranged from 0.10 - 0.12, and 1.56 - 2.36 NTD/g $\triangle$COD. Since the elimination capacity and specific cost of H_2O_2 is better than that of NaOCl, H_2O_2 was chosen and applied in the field. To prevent the remaining H_2O_2 leads to the increase of COD, control strategies of H_2O_2 addition were also established. The dosage of H_2O_2 can be calculated from the estimation of the $\triangle$COD of the wastewater, the $\triangle$COD of the wastewater can be estimated from measuring the raw wastewater conductivity. Moreover, the optimal Oxidation-reduction potential (ORP) of the wastewater should be ~50 mV; it can be treated as an indicator that reductive compounds have been fully oxidized and that little H_2O_2 remains. The signal of ORP can be fed to the system to control H_2O_2 dosing. Afterwards, both H_2O_2 oxidation technology and control strategies have been applied in the field. Thereafter, the COD of the discharged wastewater 100% meets the set value.

Keywords: Desulfurization slag, Cleaning wastewater, H_2O_2, NaOCl

1. INTRODUCTION

During steelmaking, the lime and fluorite are treated as desulfurizer to remove the sulfur in the liquid iron. The slag floating on the surface is separated and then forms desulfurization slag[1]. The major components of desulfurization slag are iron oxides, calcium oxide, and silicon dioxide[2]. The desulfurization slag can be recycled as soil improvement material, or as fine aggregate in cement-based concrete materials[3]. A desulfurization slag recycling plant was designed to separate the iron oxides from the desulfurization slag by magnetic separation, selective particle size screening and dehydration. For the plant, the discharged wastewater was around 100 cubic meters per day (CMD), and it was found that during the main separation, screening and dehydration processes, no wastewater was discharged. The wastewater almost came from cleaning of the trucks, which transport the desulfurization slag from steelmaking plant to desulfurization slag recycling plant and concrete plant. Once, it was found that the chemical oxygen demand (COD) of the wastewater occasionally exceed the set value, i.e., 480 mg/L. The cleaning wastewater treatment processes were originally designed as follows: sedimentation, pH adjustment, and then discharge to an industrial park wastewater treatment plant. To avoid the penalty, the investment on improving wastewater quality was conducted.

Oxidation is the process of losing electrons, and the opposite process, called reduction which occurs when there is a gain of electrons. The oxidation and reduction reaction can be started with an oxidant mixed with reductive compounds. Hydrogen peroxide (H_2O_2) and sodium hypochlorite (NaOCl) are two of the most common oxidants used in wastewater treatment to reduce COD[4]. The major target in this study is to find an optimal oxidant and treatment condition that reduce COD to less than 480 mg/L. Moreover, to prevent the increase of COD contributed from remaining H_2O_2, establishment of control strategies of H_2O_2 addition were expected[5].

2. EXPERIMENTAL METHOD

2.1 Water quality analysis

Cleaning wastewater, which mainly came from truck washing, was collected from the desulfurization slag recycling plant. Conductivity, pH, chloride (Cl^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}), magnesium (Mg^{2+}), COD, total organic carbon (TOC) and suspended solid

(SS) were examined. inoLab® Cond 7110 (WTW) equipped with conductivity cell Probe LR 925/01 was used to measure conductivity. PH/mV/Temperature meter SP701 (SUNTEX) equipped with pH/ORP sensor was used to measure pH and ORP. Dionex ICS-1100 (Thermal Fisher) equipped with AS22 (anion) and CS12A (cation) column was used to measure Cl^-, SO_4^{2-}, Ca^{2+}, and Mg^{2+} concentration. Potassium dichromate reflux method (NIEA W515.5A) was conducted to analyze COD. To analyze the soluble COD, a pre-filtration with 0.45 μm mixed cellulose ester membrane of the wastewater was conducted. Insoluble COD was calculated from total COD minus soluble COD. Sievers InnovOx TOC analyzer was employed to analyze TOC. Standard method of SS analysis (NIEA W210.58A) was also conducted.

2.2 Oxidation by hydrogen peroxide

As mentioned, in *2.1*, cleaning wastewater was collected from the desulfurization slag recycling plant. A proper volume of the wastewater was shaken and mixed well before being poured out, and then 25 mL of wastewater was transferred to each 100 mL beaker individually. H_2O_2 (30%) was employed for the experiments. Volume ratio of H_2O_2 (30%) and wastewater ranged from 0% to 4% were employed. It meant 0 mL to 1 mL H_2O_2 (30%) was mixed with 25 mL wastewater and stirred continuously. After 10 minutes, the pH of the wastewater was adjusted to 8.5 with 5 N HCl. Afterwards, water sample was taken and COD, ORP, and sulfate were analyzed.

2.3 Oxidation by sodium hypochlorite

Cleaning wastewater was collected from the desulfurization slag recycled plant as well. A proper volume of the wastewater was shaken and mixed well, and then 25 mL of wastewater was transferred to each 100 mL beaker individually. Sodium hypochlorite with a concentration of 10% active chlorine, abbreviated as NaOCl

(10%), was employed for the experiments. Volume ratio of NaOCl (10%) and wastewater ranged from 0% to 20% were conducted. It meant 0 mL to 5 mL NaOCl (10%) was mixed with 25 mL wastewater and stirred continuously. After 10 minutes, the pH of the wastewater was adjusted to around 8.5 with 5 N HCl. Afterwards, a water sample was taken and COD, ORP, and sulfate were analyzed.

2.4 Evaluation of treatment processes and optimal reaction time

Elimination capacity and specific cost were evaluated to compare the pros and cons between H_2O_2 and NaOCl. Elimination capacity (g $\triangle$COD/g oxidant) is the ratio of eliminated COD and the amount of oxidant added. Specific cost (NTD/g $\triangle$COD) is the ratio of the amount of oxidant cost and the eliminated COD. The cost of oxidant was based on 12.7 NTD (New Taiwan Dollar) per kilogram H_2O_2 (30%) and 30 NTD per kilogram NaOCl (10%). To obtain optimal reaction time of H_2O_2, the profile of ORP with time was conducted and it was treated as the indicator of optimal reaction time. 0.2 mL H_2O_2 (30%) was mixed with 25 mL wastewater and stirred continuously, meanwhile the ORP was recorded. After 20 minutes, the pH of the wastewater was adjusted to 8.5 with 5 N HCl. To compare with the H_2O_2 experiment, the wastewater was aerated by air (1 L air/min) as control experiment. The duration of aeration was 20 minutes, afterwards, the pH of the wastewater was adjusted to 8.5 with 5 N HCl.

3. RESULTS AND DISCUSSION

3.1 Water quality of cleaning wastewater

The cleaning wastewater treatment processes were originally designed as sedimentation, pH adjustment, and then discharge to an industrial park wastewater treatment plant. The water quality of different unit of treatment processes at the beginning of the operation are

Table 1 The results of water quality analysis in the different wastewater treatment units

Processes	pH	Conductivity (mS/cm)	Cl⁻ (mg/L)	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	COD (mg/L) Soluble	COD (mg/L) insoluble	TOC (mg/L)	SS (mg/L)
Raw wastewater	12.4	9.83	127	95	990	0	905	17	13	1,089
Sedimentation*	12.4	9.83	129	101	979	0	681	9	9.4	81
pH adjustment to 7.6**	7.6	10.01	151	98	963	4	713	11	9.6	78
Treatment with H₂O₂ and adjust pH***	8.6	12.8	148	2,042	950	3	155	9	7.8	79

*Raw water after sedimentation with a retention time of around 80 minutes

**Adjusted the pH of the wastewater after sedimentation to 7.6 with 5N HCl

***Treatment with 0.1mL 30% H_2O_2 in 25 mL wastewater after sedimentation and the adjusted pH to 8.6 with 5N HCl

shown in Table 1. The raw wastewater pH, conductivity, Ca^{2+}, COD, and SS were 12.4, 9.83 mS/cm, 990 mg/L, 905 mg/L, 1,089 mg/L, respectively. High pH and Ca^{2+} were attributed to the large amount of the CaO in the desulfurization slag. After sedimentation, SS was reduced from 1,089 to 81 mg/L, and COD was reduced from 905 to 681 mg/L. After adjusting pH to 7.6, COD remained almost constant. It revealed at the beginning of the operation, the COD may exceed the set value (480 mg/L). Since the soluble COD contributed >98% of total COD, the sedimentation and adjustment of pH will not work on COD elimination.

Moreover, high COD (713 - 905 mg/L) and low TOC (9.4 - 13 mg/L) concentration revealed that COD was caused by non-carbon-based compounds. It is assumed COD was caused by reductive-sulfur-compounds, such as $S_2O_3^{2-}$, etc. To confirm the assumption, wastewater after sedimentation was treated with 0.1mL H_2O_2 (30%) in 25 mL wastewater and then adjust pH to 8.6. The results showed sulfate increased from 98 to 2,042 mg/L, and COD decreased from 713 to 155 mg/L. It was confirmed COD was caused by reductive-sulfur-compounds, and sulfate would increase with the decrease of COD.

3.2 Feasibility of oxidation by hydrogen peroxide

Hydrogen peroxide (H_2O_2) is one of the most common oxidants used in wastewater treatment. As mentioned in the previous section, H_2O_2 has been successfully used in COD reduction. Volume ratio of H_2O_2 and wastewater ranging from 0% to 4% were conducted in this section. As shown in Figure 1, sulfate and ORP increased with the increase of volume ratio, and they kept a constant when the volume ratio was larger than 2.0%. The COD decreased with the increase of volume ratio when ranged from 0 to 0.4%. However, the COD increased with the increase of volume ratio ranged from 0.4 to 4.0%. The increased COD was caused by the remaining H_2O_2 in the wastewater. The optimal dosage of H_2O_2 was 0.4% volume ratio, and the residual COD was 155 mg/L which is less than the set value (480 mg/L).
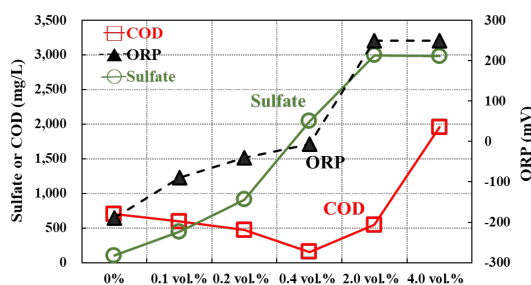

Fig.1. The results of COD, ORP, and sulfate under 0 - 4.0% volume ratio of H_2O_2 (30%) and wastewater.

3.3 Feasibility of oxidation by sodium hypochlorite

Sodium hypochlorite (NaOCl) is also one of the most common oxidants used in wastewater treatment. Volume ratio of NaOCl and wastewater ranged from 0% to 20% were conducted in this section. As shown in Figure 2, sulfate and ORP increased with the increase of volume ratio. On the contrary, the COD decreased with the increase of volume ratio. This was very different with the results that using H_2O_2 as oxidant in the previous section. The remaining NaOCl will not lead to the increase of COD. The optimal dosage of NaOCl was 8.0% volume ratio, and the residual COD was 123 mg/L which is less than the set value of 480 mg/L.
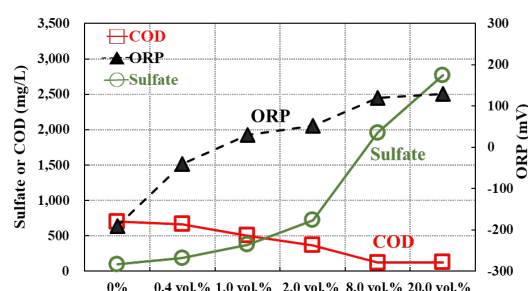

Fig.2. The results of COD, ORP, and sulfate under 0 - 20% volume ratio of NaOCl (10% active chlorine) and wastewater.

3.4 Determination of treatment process and control strategies

Elimination capacity and specific cost were evaluated to compare the pros and cons between H_2O_2 and NaOCl. Elimination capacity (g $\triangle$COD/g oxidant) is the ratio of eliminated COD and the amount of oxidant added. As shown in Table 2, the elimination capacity of H_2O_2 ranged from 0.42-0.47, and the elimination capacity of NaOCl ranged from 0.15-0.22. The capacity of H_2O_2 was larger than that of NaOCl. It was attributed to the oxidation-reduction potential of H_2O_2 being higher than that of NaOCl. Specific cost (NTD/ g $\triangle$COD) is the ratio of the amount of oxidant cost and the eliminated COD, as the results show in Table 2. The specific cost of H_2O_2 ranged from 0.10-0.12, and the specific cost of NaOCl ranged from 1.56-2.36. The using of NaOCl as an oxidant in this study was more expensive than using H_2O_2 as an oxidant. However, as mentioned in section 3.2, the remaining H_2O_2 in the wastewater would contribute COD, that leads to an increase of 0.41 g COD/g H_2O_2. In contrast, overdosing with NaOCl will not lead to the increase of COD. Since the elimination capacity and the specific cost of H_2O_2 is better than that of NaOCl, H_2O_2 was chosen and applied in the field.
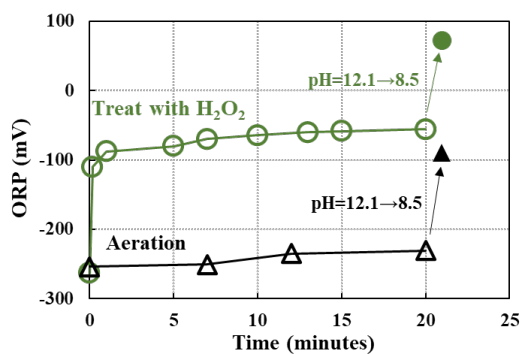
Table 2　The elimination capacity and specific cost of H_2O_2 and NaOCl

Oxidant	Elimination capacity* (g △COD/g Oxidant)	Specific cost** (NTD/g △COD)	Remark
H_2O_2	0.42~0.47	0.10~0.12	Overdosing leads to an increase of 0.41 g COD/g H_2O_2
NaOCl	0.15~0.22	1.56~2.36	Overdosing will not lead to COD increase

*Elimination capacity is the ratio of eliminated COD and the amount of oxidant added.

** Specific cost is the ratio of the amount of oxidant cost and the eliminated COD. The cost of oxidant was based on 12.7 NTD/kg H_2O_2 (30%) and 30 NTD/kg NaOCl (10%).
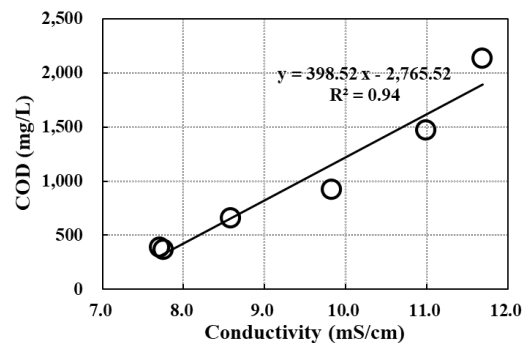
To determine optimal reaction time of H_2O_2, the profile of ORP with time was conducted and it was treated as the indicator of optimal reaction time. 0.2 mL H_2O_2 (30%) was mixed with 25 mL wastewater and stirred continuously, meanwhile the ORP was monitored. After 20 minutes, the pH of the wastewater was adjusted to 8.5 with 5 N HCl. As the results showed in Figure 3, the ORP increased dramatically once the H_2O_2 mixed with wastewater, and then ORP increased slowly with time. Afterwards, while the pH was adjusted from 12.1 to 8.5, the ORP increase from -55 to +72 mV. To compare with the H_2O_2 experiment, the 1 L air/min aeration rate of the wastewater without H_2O_2 was conduction as a control experiment. As the results showed in Figure 3, the ORP increased slowly. Afterwards, while the pH was adjusted from 12.1 to 8.5, and the ORP increase from -231 to -90 mV. From the ORP profile of the H_2O_2 treatment, optimal reaction time of H_2O_2 was set to at least 10 minutes.

>98% of the total COD. It revealed that the COD may be related to conductivity. The relationship between conductivity and COD is shown in Figure 4, a R^2=0.94 between conductivity and COD was calculated. It means we can measure the conductivity very quickly and then estimate the COD concentration through the conductivity. As we know the COD concentration, the dosage of H_2O_2 can be estimated from the elimination capacity, as shown in Table 2. In summary, the dosage of H_2O_2 can be calculated from the estimation of the △COD of the wastewater, the △COD of the wastewater can be estimated from measuring the raw wastewater conductivity. Moreover, the optimal ORP of the wastewater should be ~50 mV; it can be treated as an indicator that reductive compounds have been fully oxidized and that little H_2O_2 remains [6]. The signal of ORP can be fed to the system to control H_2O_2 dosing.

Fig.3. The profile of ORP with time for wastewater treated H_2O_2 (0.2 mL H_2O_2 (30%) react with 25 mL wastewater) and aeration (1 L air/min). The pH of the wastewater was adjusted to 8.5 with 5 N HCl at the end of the experiment.

Since the remaining H_2O_2 in the wastewater contributed to COD, the establishment of control strategies of dosing H_2O_2 would be an important issue. As we mentioned in section 3.1, COD was caused by reductive-sulfur-compounds, and the soluble COD contributed

Fig.4. The relationship between conductivity and COD of the raw wastewater.

4. CONCLUSION

A desulfurization slag recycling plant was designed to separate the iron oxides from the desulfurization slag by magnetic separation, particle size screening and dehydration. The wastewater of the plant was estimated to be around 100 CMD, with most coming from the cleaning of the trucks. However, it was found that in the beginning of the operation, the COD of the wastewater

occasionally exceeds the set value. The water quality analysis results showed the soluble COD contributed >98% of total COD, original wastewater treatment processes cannot afford to reduce COD, and COD was mainly caused by reductive-sulfur-compounds.

Two of the most common oxidants, H_2O_2 and NaOCl were employed to eliminate COD. The optimal dosage of H_2O_2 (30%) and NaOCl (10%) were 0.4%, 8.0% (volume ratio) of the wastewater, and the residual COD were 155 and 123 mg/L, respectively. The elimination capacity of H_2O_2 and NaOCl ranged from 0.42 - 0.47, and 0.15-0.22 g $\triangle$COD/g oxidant. The specific cost of H_2O_2 and NaOCl ranged from 0.10 - 0.12, and 1.56 - 2.36 NTD/g $\triangle$COD. Since the elimination capacity and the specific cost of H_2O_2 is better than that of NaOCl, H_2O_2 was chosen and applied in this field.

To prevent the remaining H_2O_2 leading to the increase of COD, control strategies of H_2O_2 addition were established. The dosage of H_2O_2 can be calculated from estimation of the $\triangle$COD of the wastewater, $\triangle$COD of the wastewater can be estimated from measuring the raw wastewater conductivity. Moreover, the optimal ORP of the wastewater should be ~50 mV; it can be treated as an indicator that reductive compounds have been fully oxidized and that little H_2O_2 remains. The signal of ORP can be fed to the system to control H_2O_2

dosing. Afterwards, both H_2O_2 oxidation technology and control strategies have been applied in the field. The cleaning wastewater treatment processes were modified to sedimentation, H_2O_2 oxidation, and pH adjustment to 7 - 8.5, and then discharge to an industrial park wastewater treatment plant. Thereafter, the COD of the discharged wastewater 100% meets the set value.

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