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Reduction of COD and Color of Acid and Reactive Dyestuff Wastewater Using Ozone

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Abstract−Wastewaters obtained from bromamine acid dye and reactive dye manufacturing were treated by ozone bubbling in a cylindrical batch reactor for the purpose of reducing COD to below 150 mg/L, which is the environmental discharge standard of the Republic of Korea. Remarkable COD reduction and decolorization were observed at pH over 11. High inlet gas flowrate and high concentration of ozone gave better results. Little precipitation was observed under the conditions of remarkable COD reduction. At pH of 11, 15 LPM of inlet gas flowrate and 89.3 g/Nm^3 of ozone flowrate, the COD of bromamine acid dyestuff wastewater was reduced to 95 mg/L after 90 minutes, and the COD of reactive dyestuff wastewater was reduced to 120 mg/L after 120 minutes. Decolorization was completed after 30 minutes of reaction.

Key words: Ozone, Dyestuff, Wastewater, Color, COD, pH

INTRODUCTION

A great deal of water is used in the dyestuff manufacturing process. Dyestuff is formulated from many kinds of chemicals, and excess chemicals are discharged as wastewater during the process. Sometimes products are discharged into the wastewater during the process of salting-out. Therefore, 15% of total amounts are lost as wastewater [Salem, 2000]. Dyestuff wastewater has a COD of 3,000-2,0000 mg/L. Not only is it directly toxic to the biological world, but it also has a dark color, which blocks sun light. By these reasons, it causes many problems to the ecosystem. However, it is very difficult to decolorize with traditional physical and chemical methods [Kuo, 1992; Kong et al., 2003]. Dyestuff wastewater is composed of many organic compounds that are difficult to treat by biological methods [Bigda, 1995; Sarasa et al., 1998]. Effective methods of decreasing COD and color are chosen depending on the type of dyestuff, and multiple processes are generally used to successfully treat the wastewater [Kuo, 1992; Li et al., 1999].

To date, coagulation methods [Han et al., 1999; Orta et al., 1998], biological methods [Kang et al., 2000; Li et al., 1999; Tatarko et al., 1998; Weber et al., 1999; Lee and Hano, 2001], adsorption methods [Cooney, 1999; Lee et al., 1997; Markovska et al., 2001; Weber et al., 1999; Hur and Kim, 2000], chemical methods [Kang et al., 2000; Kuo, 1992; Park et al., 1999; Salem et al., 2000; Weber et al., 1999] and membrane separation methods [Weber et al., 1999] have been used to treat dyestuff wastewater. Coagulation is effective for treatment of insoluble dyestuff wastewater but not so effective for soluble dyestuff wastewater [Kang et al., 2000; Kuo, 1992]. The biological method has difficulty finding the proper micro-organisms which can withstand toxicity of the dyestuff wastewater [Ince, 1999; Kang et al., 2000; Kuo, 1992; Weber et al., 1999]. The adsorption method has difficulties in the treatment of insoluble dyestuff wastewater and it is very difficult to find the desorption process [Kuo, 1992; Kim et al., 2002]. The membrane separation method has problems in that the pore is filled with the particles, so the membrane lifetime is very short [Weber et al., 1999]. The chemical method is to oxidize organic materials by oxidizing agents. Fenton's method is the representative chemical method that uses H_2O_2 and iron catalysts. Most factories use this method to reduce COD and color. But, it cannot satisfy the environmental discharge standard by itself alone and the cost is relatively high. The evaporation method is the most ideal method ever developed, but it has high operating cost.

An ozone method is one of the chemical methods, and it is used as an oxidizing agent instead of H_2O_2. The ozone method is known to be effective for decomposing organic chemicals containing carbon-carbon double bonds, olefinic double bonds, acetylenic triple bonds, aromatic compounds, phenols, polycyclic aromatics, heterocyclics, carbon-nitrogen double bonds, carbon-hydrogen bonds, silicon-hydrogen and carbon-metal bonds [Evans, 1975]. Most of the dyestuffs are composed of aromatic organic compounds, so the ozone method is getting attention with the prediction that it could decompose various kinds of dyestuffs. It is reported that the ozone is effective for reducing the color of dyestuff wastewater, but it is not so effective for the COD reduction [Churchley, 1998; Kuo, 1992; Sarasa et al., 1998]. Therefore, most studies for dyestuff wastewater treatment with ozone have been interested in decolorization rather than COD reduction. It has been emphasized that the ozone works as a catalyst for the physical and chemical treatment [Orta et al., 1998].

This aim of this study was to show that the ozone method is effective for the reduction of COD as well as decolorization of dyestuff wastewater, to present the optimum conditions for dyestuff wastewater treatment and to present the design parameters for scale-up. COD reduction of dyestuff wastewater below 150 mg/L, which is the environmental discharge standard of the Republic Korea, was

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the object of this study. Raw dyestuff wastewaters obtained from the Daekwang Chemical Co. at Namdong industry complex in Inchon were used for the experiments. The wastewater was treated by bubbling ozone in the cylindrical type batch reactor. The COD, color and pH of sample were analyzed, taking the concentration of ozone, the flowrate of inlet gas and the pH of sample as variables.

EXPERIMENTS

Wastewater contains various kinds of dyestuff, and it is difficult to identify the components precisely. The major components could be determined by investigating the major dyestuffs. Bromamine acid dyestuff wastewater and reactive dyestuff wastewater were used in this experiment. These dyestuffs have relatively high solubility according to the low molecular weight. Insoluble components can be removed easily by a physical method such as the coagulation process. In the case of raw acid dyestuff wastewater, the COD was 3,240 mg/L, pH was 3.7, and maximum absorbance was 11.1 at the wavelength 442 nm. In the case of raw reactive dyestuff wastewater, the COD was 2,560 mg/L, pH was 4.1, and maximum absorbance was 6.3 at the wavelength of 400 nm. 45% NaOH solution was used to adjust the pH of samples.

Oxygen of 99.7% purity was used to generate ozone. Ozone was generated by flowing the oxygen into the ozone generator (Ilssan, 3E3G ozone generator). Ozone concentrations at different O_2 flowrates are listed in Table 1, and ozone concentrations at different output voltages are listed in Table 2. Ozone was contacted with the dyestuff wastewater in the cylindrical type batch reactor (length: 1,000 mm, I.D.: 60 mm) by bubbling. The reactor was made of acryl to keep away from the oxidation and to observe the change of the color easily. A ceramic air distributor (O.D.: 40 mm) was located at the bottom of the cylinder and the ozone bubble was generated from the distributor. The experimental set-up is shown in Fig. 1.

The pH, absorbance and COD of dyestuff wastewater were measured after filtration. The pH was measured with a pH meter (Orion 410A), and the absorbance was measured with a UV/VIS spectrophotometer (Beckman DU-650). The potassium permanganate method was used to measure the COD because the environmental discharge standard of the Republic of Korea prescribes it. COD of dyestuff wastewater of high concentration was measured by basic potassium permanganate method because of the high quantity of chlorine ions in the sample. After the ozone treatment, COD was measured by acidic potassium permanganate method.

Table 1. Characteristics of ozone concentration according to the O_2 flow rate (output voltage: 12 kV)

O_2 flow rate (LPM)	O_3 concentration (g/Nm^3)	O_3 amount (g/hr)
10.0	102.2	61.3
12.5	96.0	72.0
15	82.7	74.4

Table 2. Characteristics of ozone concentration according to the output voltage (feed flowrate: 15 LPM)

Output voltage (kV)	O_3 concentration (g/Nm^3)	O_3 amount (g/hr)
9	54.0	48.6
10	68.8	61.9
11	76.5	68.9
12	82.7	74.4

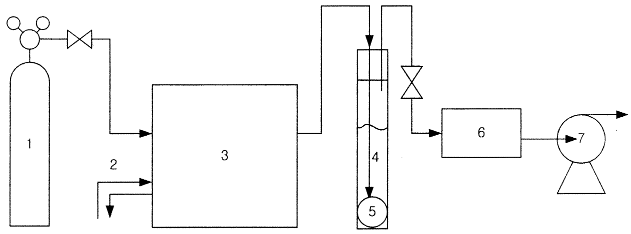

Fig. 1. Schematic diagram of experimental system for the treatment of dyestuff wastewater with ozone.
1. O_2 cylinder
2. Cooling water
3. Ozone generator
4. Sample
5. Gas disperser
6. Ozone detector
7. Gas inspirator

RESULTS AND DISCUSSION

1. Effect of pH in Ozone Treatment

The pH of raw acid dyestuff wastewater was 3.7 and that of raw reactive dyestuff wastewater was 4.1. The COD of acid dyestuff wastewater was reduced from 3,240 mg/L to 1,520mg/L after ozone bubbling treatment for 2 hr. The COD of reactive dyestuff wastewater was reduced from 2,560 mg/L to 1,120 mg/L at the same condition. When the pH was changed to 7.0, the COD of acid dyestuff wastewater was reduced to 710 mg/L and that of reactive dyestuff wastewater was reduced to 986 mg/L. With the idea that the difference of the results came from the difference of the pH of samples, ozone treatment experiments were performed with various pH of samples. The COD after ozone treatment was measured at

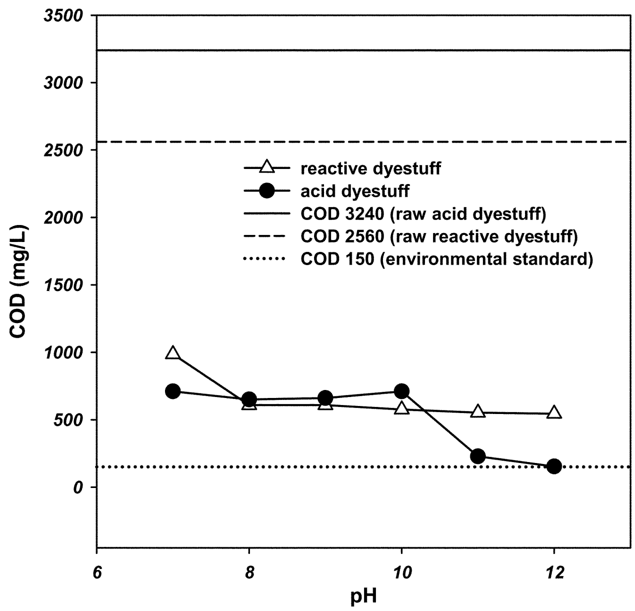

Fig. 2. The reduction of COD after ozone treatment according to the changes of pH.

the various pH of 7-12, and the results are shown in Fig. 2. Reaction time of 120 min, sample volume of 500 ml, output voltage of 12 kV and inlet gas flowrate of 12.5 LPM was fixed in this experiments.

In the case of reactive dyestuff wastewater, the COD decreased slightly with all pH. With acid dyestuff wastewater, the COD decreased slightly at pH 7-10, and it decreased greatly to 228 mg/L showing a reduction rate of 93% at pH 11. The COD decreased to 153 mg/L at pH 12 showing a reduction rate of 95%.

Acid dyestuff wastewater was observed to be sensitive to pH variation. With the result of acid dyestuff wastewater, there was a possibility that the COD reduction would be effective at high pH. 45 ml of 45% NaOH solution was needed to adjust pH 11 with 30 liters of dyestuff wastewater. 70 ml of 45% NaOH solution was needed to adjust pH 12. When the pH was changed from 11 to 12, the reduction rate of COD was changed from 93% to 95%. This meant that the increase of NaOH solution does not affect the COD so much. It was decided that the optimum pH would be 11.

In Fenton's method OH radical acts as an oxidant. The OH radical appears to be active in the low pH conditions of 3-5. Therefore, low pH has been reported to be effective with Fentons method [Kang et al., 2000; Kuo, 1992; Park et al., 1999; Weber et al., 1999]. On the contrary, high pH has been reported to be effective with the ozone method [Sarasa et al., 1998]. In the ozone method, oxygen radicals and ozone molecules act as an oxidant. The ozone radical appears to be active at basic pH condition, and this is because of the OH^-.

When the pH of sample was compared before and after the ozone treatment, the pH was reduced for all pH ranges as shown in Fig. 3. In the case of the reactive dyestuff, the OH^- changes to OH radical and effectively is used to react with the dyestuff. A remarkable amount of precipitation was observed after the reaction with pH variation. In the case of acid dyestuff wastewater, a large quantity of brown precipitation was detected up to pH 10, but little colorless precipitation was detected from pH 11. For reactive dyestuff wastewater, brown precipitation was detected under all conditions. In general, COD was reduced remarkably under the conditions showing little precipitation after reaction. It is reported that the production of precipitation during the wastewater treatment is helpful to the reduction of COD [Kuo, 1992].

Theoretically, if a complete reaction would be possible, organic compounds composing dyestuff wastewater completely decompose to H_2O and CO_2 [Bigda, 1995; Lang et al., 1998; Rinker et al., 1999]. However, complete decomposition is not so easy. Therefore, remaining compounds could be eliminated by precipitation. For Fenton's method, it is reported that ozone is helpful for dyestuff wastewater treatment by filtration after precipitation [Kuo, 1992]. It is also reported that ozone is helpful for deducing coherent material during the coagulation process. Ozone could make particle size large, so dyestuff water could be filtrated easily [Orta et al., 1998]. However, the results of this study for ozone method led to the opposite conclusion that the COD reduction was remarkable with little precipitation at pH 11. Therefore, most of the organic compounds in dyestuff wastewater were supposed to be decomposed to CO_2 and H_2O.

2. Effect of Ozone Flowrate

Experiments were performed at different oxygen flowrate under pH 11. Reaction time of 120 min, sample volume of 500 ml, output voltage of 12 kV and pH of 11 was fixed. Inlet gas flowrate was changed from 12.5 LPM to 15 LPM, and the results are shown in Fig. 4.

When the inlet gas flowrate was 12.5 LPM, the volume of bubble was 5 times larger than the volume of sample with the acid dyestuff wastewater, and it was 1.5 times with the reactive dyestuff wastewater. When the oxygen flow rate was 15 LPM, the volume of bubble was similar to the case of 12.5 LPM in the acid dyestuff wastewater, and it was 5 times with the reactive dyestuff wastewater. The bubbles settled down after 15 min of reaction. The COD of

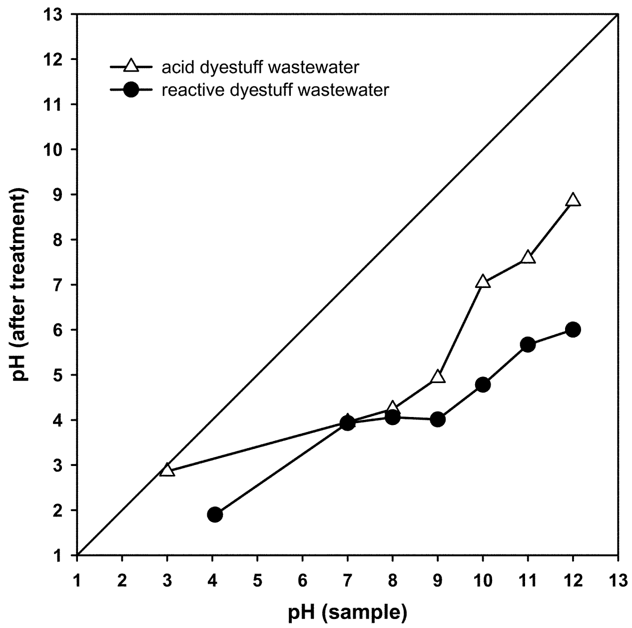

Fig. 3. The comparison of pH between the before-treatment and after-treatment samples with ozone.

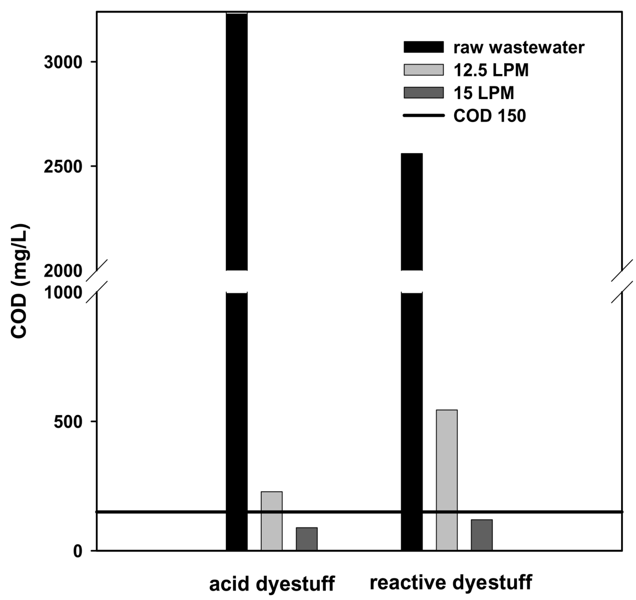

Fig. 4. The reduction of COD after the treatment depending on the O_3 flowrate (LPM).

acid dyestuff wastewater was reduced to 228 mg/L, which was 93.0% reduction, at 12.5 LPM of inlet gas flowrate. It was reduced to 89 mg/L, which was 97.3% reduction, at 15 LPM. The COD of the reactive dyestuff wastewater reduced to 544 mg/L, which was 78.8% reduction at 12.5 LPM. It was reduced to 120 mg/L, which was 95.3% reduction, at 15 LPM. The COD of the acid dyestuff wastewater reduced better than that of the reactive wastewater. The difference was large at 12.5 LPM of inlet gas flowrate. The COD of both samples reduced to below 150 mg/L, which is the environmental discharge standard of the Republic of Korea. The COD was reduced remarkably at high concentration of ozone.

With the acid dyestuff wastewater, little precipitation was detected at 12.5 LPM and 15 LPM of inlet gas flowrate. With the reactive dyestuff wastewater, little precipitation was detected at 15 LPM, but brown precipitation was detected at 12.5 LPM.

The pH of the acid dyestuff wastewater was adjusted to 11 at the beginning of the experiment, and it changed to 7.6 at 12.5 LPM and to 7.1 at 15 LPM. The pH of reactive dyestuff wastewater changed to 5.7 at 12.5 LPM and to 4.6 at 15 LPM.

3. Effect of Ozone Concentration

An experiment was carried out under various ozone concentrations of 54.0-82.7 g/Nm^3. The working volume was 500 ml, pH was 11, and inlet gas flowrate was 15 LPM. Reaction time was adjusted from 120 to 184 min at different ozone concentrations to make 149 g of total ozone.

The results are shown in Fig. 5. The COD of the acid dyestuff wastewater was reduced to 700 mg/L at 9 kV of output voltage and 54.0 g/Nm^3 of ozone concentration. It was reduced to 89 mg/L at 12 kV and 82.7 g/Nm^3.

The COD of reactive dyestuff wastewater was reduced to 746 mg/L at 9 kV of output voltage and 54.0 g/Nm^3 of ozone concentration. It was reduced to 120 mg/L at 12 kV and 82.7 g/Nm^3. The results showed that a high ozone concentration with the same total amount of ozone gave a high COD reduction rate.

Brown precipitation was detected at 9 and 10 kV, and negligible amount of precipitation was detected at 12 kV. The pH of the acid dyestuff wastewater shifted to 7.6 at 12 kV. The pH of the reactive dyestuff wastewater shifted to 4.6 at 12 kV.

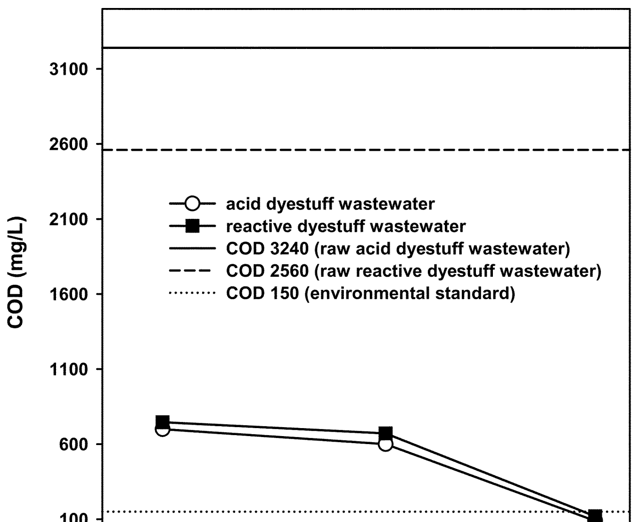

Fig. 5. The effect of ozone concentration on the reduction of COD.

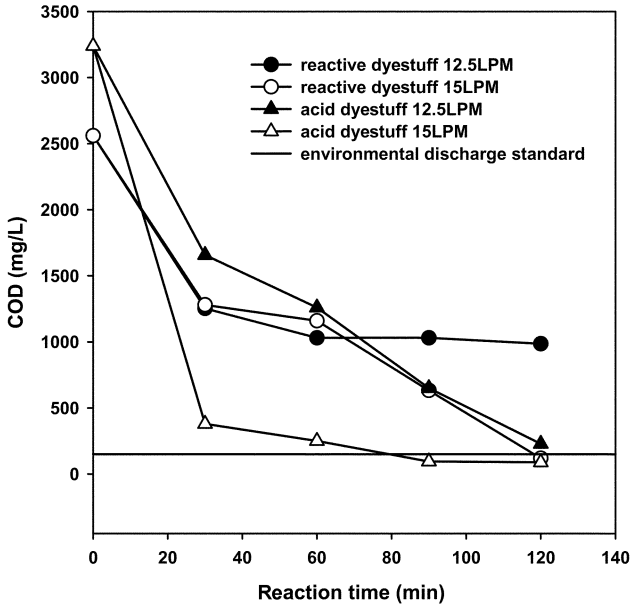

Fig. 6. The time-on stream of the COD reduction during the ozone treatment.

4. Effect of Reaction Time

According to previous experiments, high pH, high inlet gas flowrate and high ozone concentration were required for the effective treatment of the dyestuff wastewater by ozone. To find the optimum reaction time, experiments were performed with an inlet gas flowrate of 12.5 LPM and 15 LPM and the reaction time was 120 min. The sample volume of 500 ml, output voltage of 12 kV and pH of 11 were fixed. The results are shown in Fig. 6.

The COD reduction was remarkable at 15 LPM of inlet gas flowrate compared to 12.5 LPM. Treatment of the acid dyestuff wastewater with Fenton's method reduced the COD to 400 mg/L. Ozone treatment with 15 LPM for 30 min gave better result than Fenton's method. The COD of the acid dyestuff wastewater reduced to 95 mg/L after 90 min. The COD of the reactive dyestuff wastewater reduced to 120 mg/L after 120 min. The optimum reaction times to meet the environmental discharge standard were 90 min for the acid dyestuff wastewater and 120 min for the reactive dyestuff wastewater. The COD reduction of the acid dyestuff wastewater was more remarkable than that of the reactive dyestuff wastewater.

In the case of the acid dyestuff wastewater with 12.5 LPM, brown precipitation was detected up to 90 min, but it disappeared after 120 min. The precipitation was not detected after 30 min at 15 LPM. In the case of the reactive dyestuff wastewater with 12.5 LPM, brown precipitation was detected at 120 mim, but it was not detected after 90 min at 15 LPM.

The pH of the acid dyestuff wastewater shifted to 7.1 after 120 min at 15 LPM. The pH of the reactive dyestuff wastewater shifted to 4.5 after 120 min at 12.5 LPM and shifted to 4.7 after 120 min at 15 LPM.

5. Decolorization

Decolorization experiments were performed at the condition of remarkable COD reduction. Absorbance was measured at 400-800 nm wavelength with 1 nm resolution and every 5 min for 30 min. Sample volume of 500 ml, output voltage of 12 kV, pH of 11 and oxygen flow rate of 15 LPM were fixed during the experiments.

The color of the dyestuff is mainly due to the aromatic covalent bonding [Nam et al., 1998]. Ozone is excellent in the decomposition of aromatic covalent compounds, and it is good for the decolorization of the dyestuff wastewater [Evans, 1975; Sarasa et al., 1998].

Raw dyestuff wastewater samples had dark black color. Both acid and reactive dyestuff wastewaters were decolorized remarkably with ozone treatment. Transparent yellow color was observed after 15 min of reaction. Decolorization was completed in about 30 min. The absorbance of the acid dyestuff wastewater is shown in Fig. 7 and that of the reactive dyestuff wastewater in Fig. 8. The change of the absorbance of the acid dyestuff wastewater with time at 442 nm is listed in Table 3, and that of the reactive dyestuff wastewater at 400 nm is shown in Table 4. The reduction of the absorbance of the acid dyestuff wastewater was 98.4% and that of the reactive dyestuff wastewater was 95.7% after 30 min of reaction.

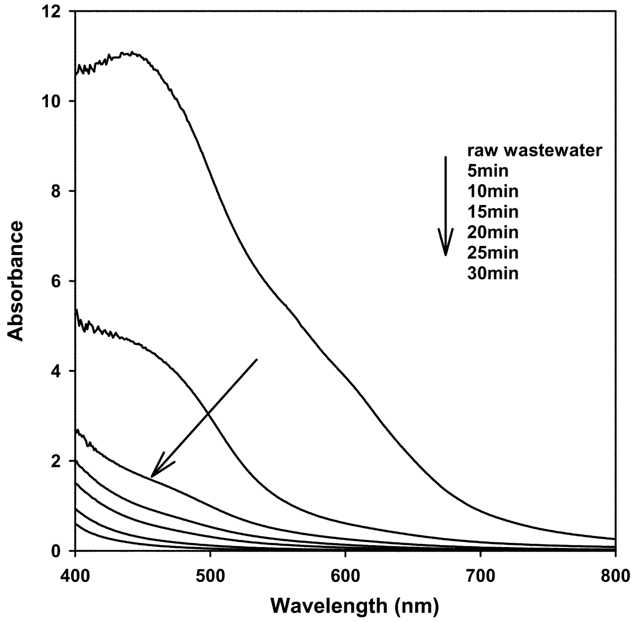

Fig. 7. The changes of the absorbance of acid dyestuff wastewater with time.

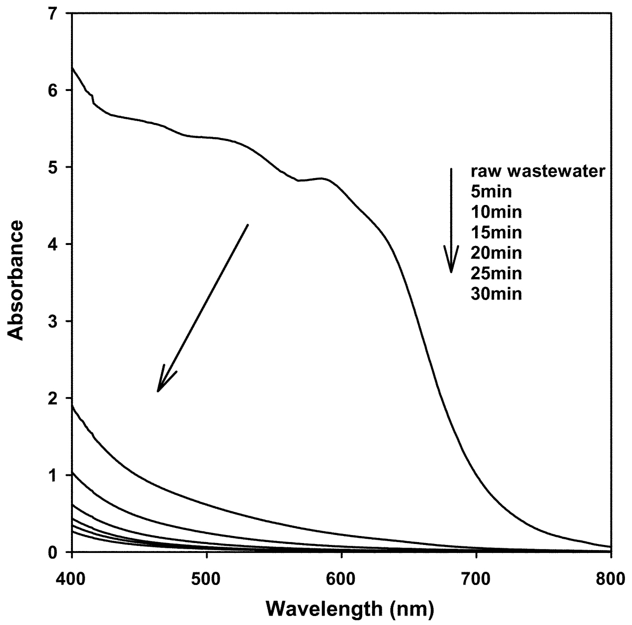

Fig. 8. The absorbance change of reactive dyestuff wastewater with time.

Table 3. Absorbance reduction of acid dyestuff wastewater (wavelength 442 nm)

Time (min)	Absorbance	Absorbance reduction (%)
Raw wastewater	11.1	
5	4.7	57.9
10	1.8	84.1
15	1.1	90.3
20	0.71	93.6
25	0.34	96.9
30	0.18	98.4

Table 4. Absorbance reduction of reactive dyestuff wastewater (wavelength 442 nm)

Time (min)	Absorbance	Absorbance reduction (%)
Raw wastewater	6.3	
5	1.9	69.8
10	1.0	83.5
15	0.62	90.1
20	0.44	93.0
25	0.35	94.4
30	0.27	95.7

CONCLUSIONS

A study of dyestuff wastewater treatment using ozone was performed. The results with the acid and the reactive dyestuff wastewater showed that COD reduction and decolorization were remarkable under the basic condition of pH 11. A large amount of bubbles was formed at high inlet gas flowrate. High ozone concentration was effective for the reduction of COD. Precipitation was not observed under the conditions of high COD reduction. The COD of the acid dyestuff wastewater was reduced to 95 mg/L after 90 min of reaction, and that of reactive dyestuff wastewater was reduced to 120 mg/L after 120 min of reaction, which satisfied the environmental discharge regulation. The pH was 11, and the inlet gas flowrate was 15 LPM with 89.3 g/Nm^3 of ozone concentration. After 30 min of ozone treatment, decolorization was completed. From these results, the ozone treatment of the dyestuff wastewater in both COD reduction and decolorization was excellent.

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