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DECOLORIZATION OF TEXTILE WASTE EFFLUENTS BY OZONATION*

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ABSTRACT

Bench experiments were conducted to investigate the efficiency of ozonation in removing the color (turbidity) and chemical oxygen demand of the textile waste effluents. It has been observed that six hours of ozonation are sufficient to remove most of the color in the waste effluent and up to 50 percent of its COD. The small molecule organic compounds produced by dye decomposition, which contribute significantly to the final COD concentration in the ozonation process, can be easily degraded in an activated sludge process. Combining ozonation and the activated sludge process can provide a very effective means for dealing with this particular type of industrial waste effluent.

INTRODUCTION

Textile manufacturing industries in Taiwan are major industrial water users. A typical dyeing plant often generates approximately seventy tons of waste effluents per 1000 yards of fiber processed. The effluents are very difficult to treat satisfactorily because they are highly variable in composition [1]. Common methods employed for treatment include biological (activated sludge), physical, and chemical processes [1-9]. Activated sludge treatment, the most widely used

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method, primarily relies on the microorganisms in the effluents to break down the dyestuffs. Because dyestuffs are complexly structured polymers not easily degraded biologically, this and similar methods are not very satisfactory. Moreover, the cost of textile waste treatment is increasing rapidly, prompting efforts to identify new, more efficient, treatment methods in an attempt to lower treatment costs and adverse environmental impacts.

This study investigates the efficiency of ozonation in decolorization of the textile waste effluents. Decolorization is generally considered to be an integral part of the textile waste treatment process. The strong color of textile waste effluents, if not properly dealt with, can have serious adverse impacts on the aquatic environment as a result of turbidity and high pollutant concentrations. Ozonation has undergone recent trials for this purpose [11-13]. However, although these studies have shown the potential of this treatment method, they have not provided sufficient information for identifying its advantages and limitations. The purpose of the present investigation is to gather experimental data in a laboratory ozonation system in an attempt to address these questions.

CHARACTERISTICS OF TEXTILE WASTE EFFLUENTS

The fibers used in the textile industries can be divided into two types: natural and man-made. The two major natural fibers are wool and cotton. The important man-made fibers include polyester, rayon, nylon, polyacrylic, and polyamide. Tables 1 and 2 show typical waste characteristics of cotton and several man-made

Table 1. Cotton Processing Waste Characteristics [1].

Process	BOD, ppm	pH	Total Solids, ppm
Slashing/sizing	620 - 2500	7.0 - 9.5	8500 - 22600
Desizing	1700 - 5200		16000 - 32000
Kiering	680 - 2900	10.0 - 13.0	7600 - 17400
Scouring	50 - 110		
Bleaching	90 - 1700	8.5 - 9.6	2300 - 14400
Mercerizing	45 - 65	5.5 - 9.5	600 - 1900
Dyeing:			
Aniline Black	40 - 55		600 - 1200
Basic	100 - 200	6.0 - 7.5	500 - 800
Developed colors	75 - 200	5.0 - 10.0	2900 - 8200
Direct	220 - 600	6.5 - 7.6	2200 - 14000
Indigo	90 - 1700	5.0 - 10.0	1100 - 9500
Naphthol	15 - 675	5.0 - 10.0	4500 - 10700
Sulfur	11 - 1800	8.0 - 10.0	4200 - 14100
Vats	125 - 1500	5.0 - 10.0	1700 - 7400

Table 2. Characteristics of Several Man-Made Textile Wastes [1]

			Solids, ppm	
Fibers/Operations	BOD, ppm	pH	Dissolved	Suspended
Acrylics				
Scouring	350	8.8	3,400	15,600
Softening	13	7.4	600	1,400
Dyeing, basic	208	8.3	500	6,000
Dyeing, acid	610	4.3	1,600	9,200
Rayon				
Boiling-off	240	3.9	1,500	32,200
Dyeing	50	7.1	2,700	150,000
Rayon-Nylon (50/50 blend)				
Scouring	585	8.2	74,000	306,000
Dyeing	123	3.5	1,400	89,000
Fixing	112	7.0	16,900	83,300
Nylon				
Scouring	2,260	-	-	-
Dyeing	675	7.6	100	26,600

fibers [1]. It is apparent from these tables that most of the textile effluents do not have very high BOD content, but do have very high total solids concentrations and large pH variation. The normal dyeing operations of a textile plant are such that the dye used varies from day to day, and even several times a day, primarily because of customers' requirements. Dye changes cause considerable variation in the waste characteristics, particularly pH. Large pH variation is especially troublesome because the pH tolerance of conventional biological treatment systems is very limited. Hence, without proper pH control, normal operation of biological treatment is essentially impossible.

Along with the high pH variation, the textile waste effluents have high temperatures. In several steps of the operation, hot rinsewaters of 80° or 90°C are used, resulting in a final effluent temperature between 35° and 40°C. This necessitates proper heat dissipation of the hot effluent prior to activated sludge treatment. But the component of the textile waste effluent which is most difficult to treat is the strong color. The combination of strong color and high dissolved solid content leads to high turbidity of the waste effluent. The dyestuffs are complex polymers which are very difficult to decompose biologically. Hence, there is little decomposition of these molecules in the activated sludge process. A strong effluent color, if not removed, may cause considerable disturbance to the ecological system of the receiving water. Color removal capabilities of activated carbon, hydrogen peroxide, and other decolorizing agents are well known. However,

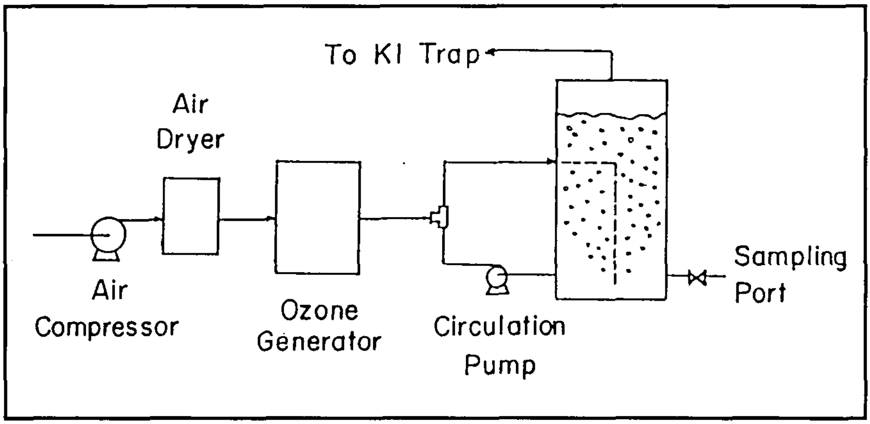


Figure 1. The schematic of experimental setup.

polishing processes using those chemicals are expensive. Ozonation is a technique that has been suggested in the literature as a potential alternative.

MATERIALS AND METHODS

The present experimental studies were conducted in a batch reactor system. The experimental schematic is shown in Figure 1. Filtered and dried ambient air (to a dew point of -55°C) was used as the feed gas. The dry, clean air was then fed to the Welsbach T816 ozone generator (Polymatrics Corporation, San Jose, California). The output from the ozone generator contained approximately 1 percent ozone. The capacity of the Welsbach ozone generator was rated as 8 g/hr. The ozone/air mixture from the ozone generator was mixed with textile waste effluent in a T-shaped aspirator and the ozonated effluent was then pumped to the bottom of the reactor. The gas/liquid mixing in the external aspirator generated very fine gas bubbles smaller than those by a ceramic sparger and provided excellent ozone absorption in the reactor. The gas effluent from the reactor was passed through a KI solution for absorption and determination of the amount of unused ozone (see Figure 1).

The textile waste effluent was obtained from a large dyeing and finishing plant. In most of the experimental runs, it was very difficult to determine what type of dyestuffs was in the waste effluent because very often several dye waste effluents were mixed together in the storage tank. The raw effluent obtained was filtered first to remove the large suspended particles. Five liters of the filtered effluent were placed in the reactor for each ozonation experiment. Liquid samples were taken periodically during each run and the COD and liquid turbidity were measured to monitor their changes during the ozonation period. Also measured were the suspended solids concentration and pH in each run. The ozone concentrations in the gases exiting the ozone generator and the reactor were also measured. This would enable determination of the amount of ozone absorption by the textile waste effluent.

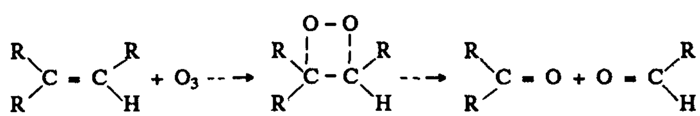
RESULTS AND DISCUSSION

To control pH in the waste, acidic and basic effluents are stored in separate tanks. They are then mixed in proper proportions in an equalization tank to adjust the pH before being sent for activated sludge treatment. Hence, the raw waste had a relatively narrow pH range between 6 and 8, in contrast to that of the effluent from the dyeing process (fluctuating between 2 and 13).

The color of the waste effluent appears to be the most difficult parameter to control due to a large number of dyestuffs being used. Hence, the effluent color could change daily or even hourly, leading to different characteristics for each batch of raw effluent collected for the experiment. Regardless of its color or turbidity, the waste effluent could be generally divided into high strength and low strength types according to its COD content. The high strength waste effluents had a COD concentration close to 2000 mg/l; low strength concentrations were near or below 800 mg/l. These two waste effluents are treated separately in the plant. Both waste effluents were considered in the present ozonation studies.

COD Reduction

Most of the dyestuffs contain straight and unsaturated bonds which are easily oxidized and decomposed by ozone. Oxidation of the unsaturated bonds will cause the COD concentration of the waste effluent to decrease. Oxidation reactions can generally be represented by



OZONIDE KETONE ALDEHYDE

in which ozonide is an unstable intermediate compound which decomposes further to ketones, aldehydes, oxalic acids, and acetic acids [14]. The small molecule final products of ozonation still possess significant amounts of COD. Hence, the COD concentration of dye waste effluents can only be reduced to a certain extent, and further COD reduction by ozonation alone is very difficult, if not impossible. Fortunately, the small molecule organic products of dye waste ozonation are amenable to biological digestion. Therefore, ozonation followed by activated sludge treatment appears to provide an excellent combination for treating the dye waste effluents.

Typical COD reductions of high strength waste effluent as a function of ozonation time are shown in Figures 2 and 3. The initial COD concentrations for both

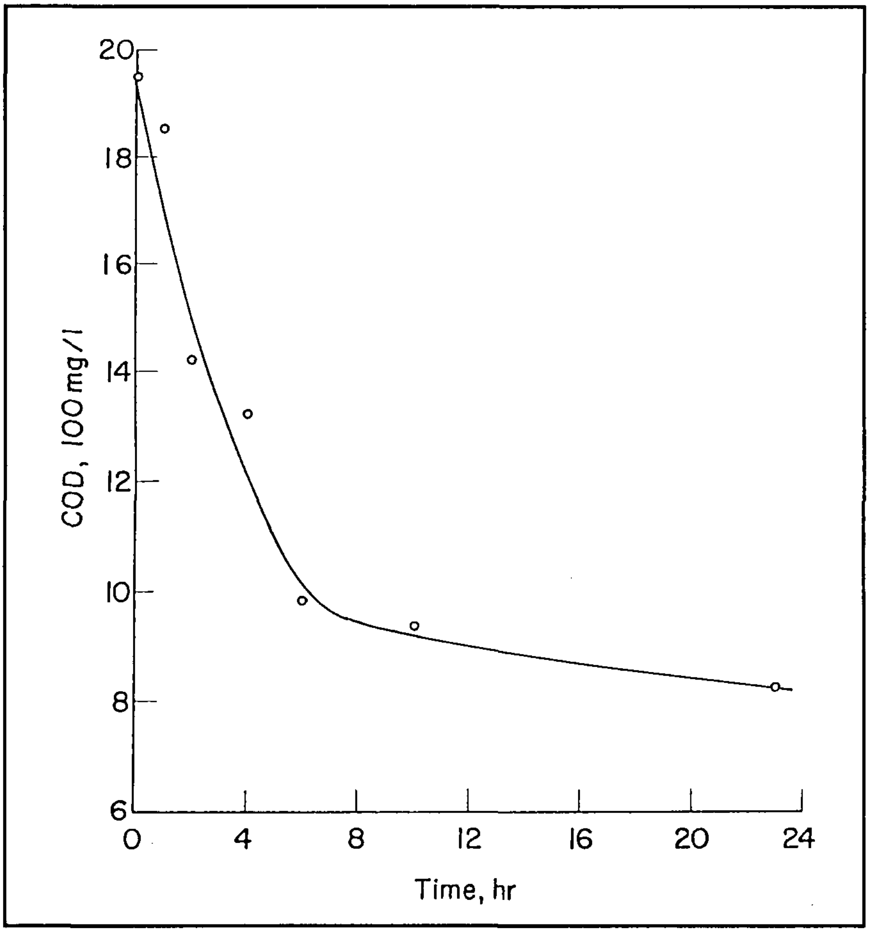


Figure 2. The first COD change of high strength textile waste effluent during ozonation.

cases were approximately 2000 mg/l. The COD decrease is rapid in the first six hours and its reduction is approximately 50 percent; after this time, the rate of COD reduction decreases. This is because of the fact that the COD decrease due to dyestuff decomposition is compensated by the COD increase due to the small molecule final decomposition products, as mentioned earlier. This postulation is substantiated by the disappearance of the effluent color.

The low strength waste effluent shows significantly lower initial COD concentration (Figures 4 and 5). The rapid COD decrease in the first six hours is apparent in these two figures. The general COD reduction is approximately 50 percent which is about the same as observed in ozonation of the high strength

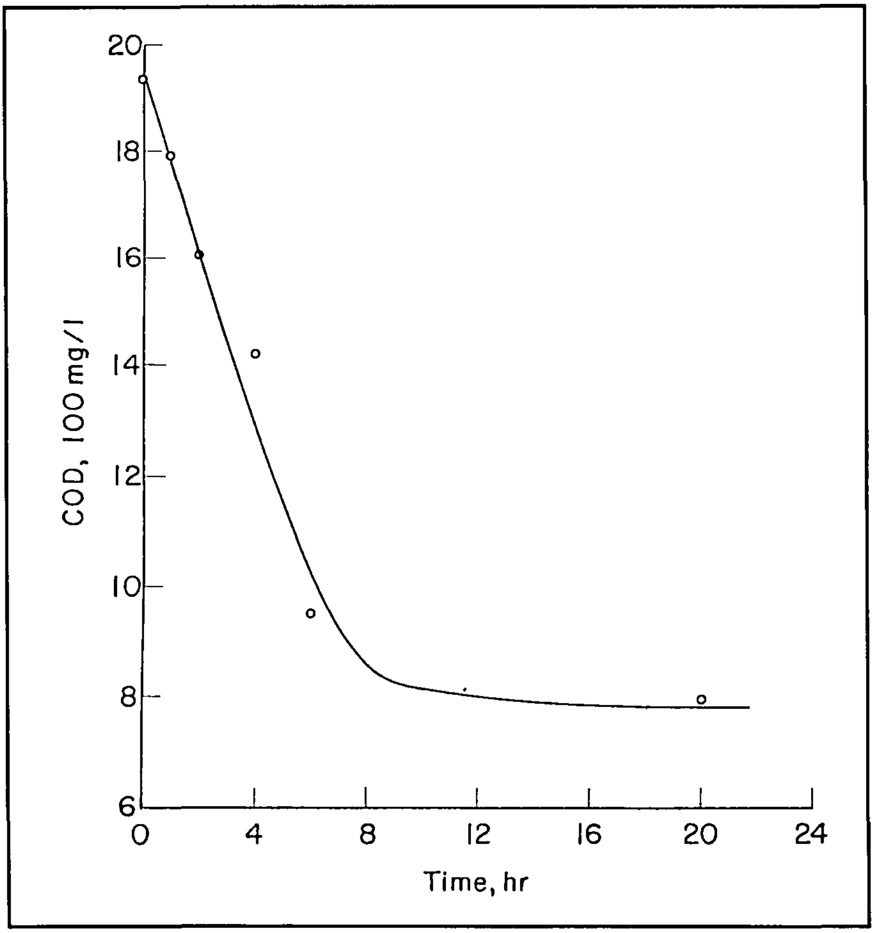


Figure 3. The second COD change of high strength textile waste effluent during ozonation.

waste effluent. From the above results, it can be concluded that ozonation of the dye waste effluents should not last more than six hours with an expected overall COD reduction of approximately 50 percent. Further ozonation does not appear to be cost-effective.

Based on the difference between the amount of ozone generated by the ozone generator and the remaining amount of ozone in the gas exiting the reactor, the rate and the amount of ozone absorbed by the dye waste effluent was determined. This amount of ozone absorption can be correlated to the percent COD reduction, as shown in Figure 6. Apparently there is little difference in the relation between the COD removal and the amount of ozone absorbed for both high strength and

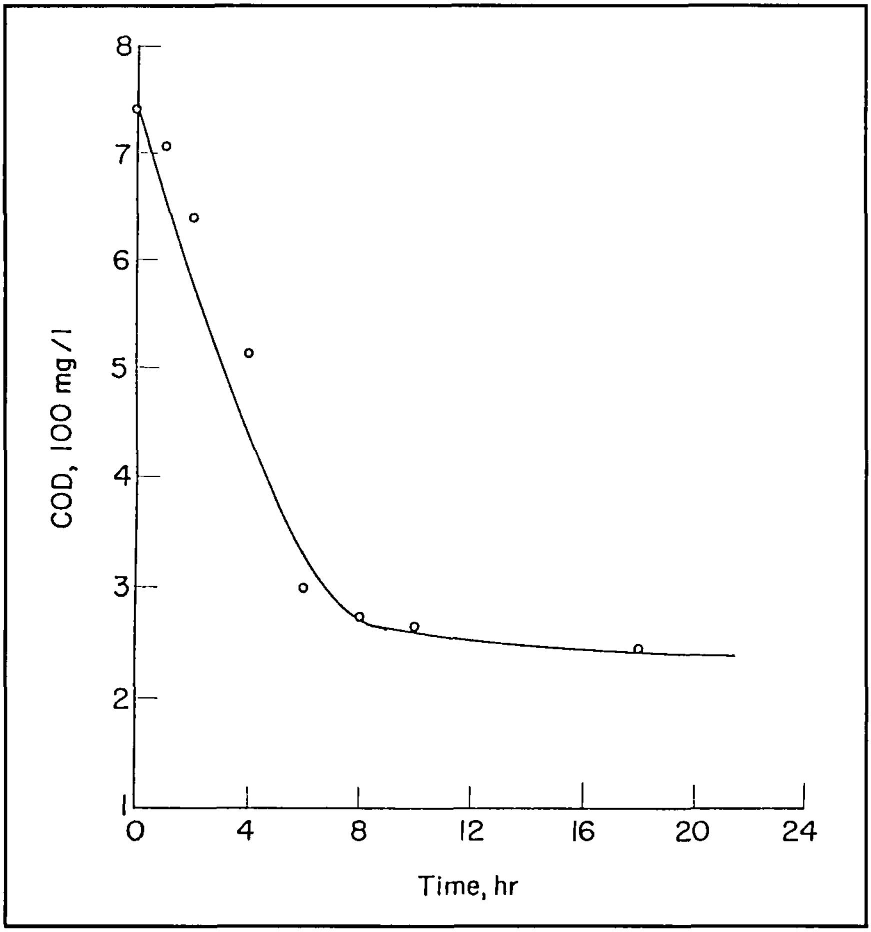


Figure 4. The first COD change of low strength textile waste effluent during ozonation.

low strength textile waste effluents. According to the general trend of these two curves, the COD removal trends to level off as more ozone is absorbed.

Color or Turbidity Reduction

During the period of the experiment, the effluent varied considerably in color and in intensity. Most of the time, the waste effluent was either dark red or brown. On several occasions, it was dark grey. The strength of waste effluent can be visibly ascertained by the color intensity. Since the turbidity of the waste effluent

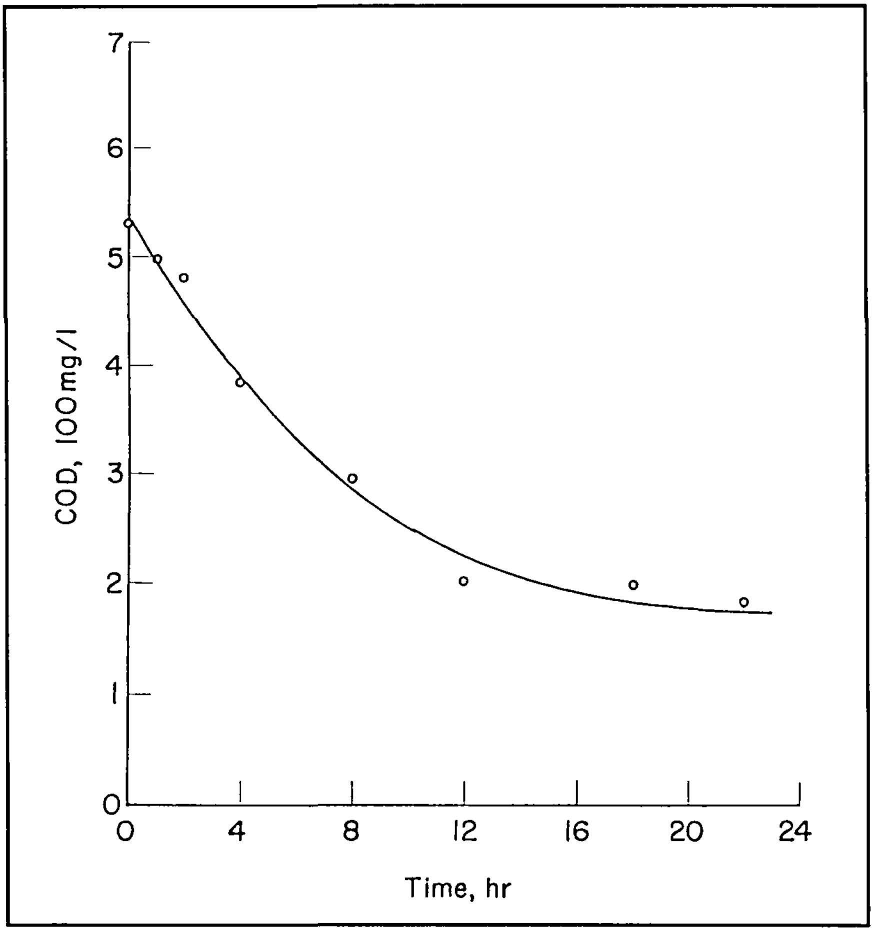


Figure 5. The second COD change of low strength textile waste effluent during ozonation.

is closely related to the color, the two quantities are considered equivalent in the experimental measurements.

The turbidity of the dye waste effluent was measured by the nephelometric method and the visual method [15]. An apparatus similar in basic structure to the candle turbidimeter was used for determining the modified Jackson turbidity unit (JTU) [15]. The measured JTU change (in centimeters) of the high and low strength dye waste effluents are shown in Figures 7 and 8, respectively. The lower initial JTUs reflect the high turbidity of the original dye waste effluents. As the ozonation progressed, the waste effluent improved significantly in visibity and, hence, in higher JTUs. At the JTU around 8, the waste effluent turned lightly

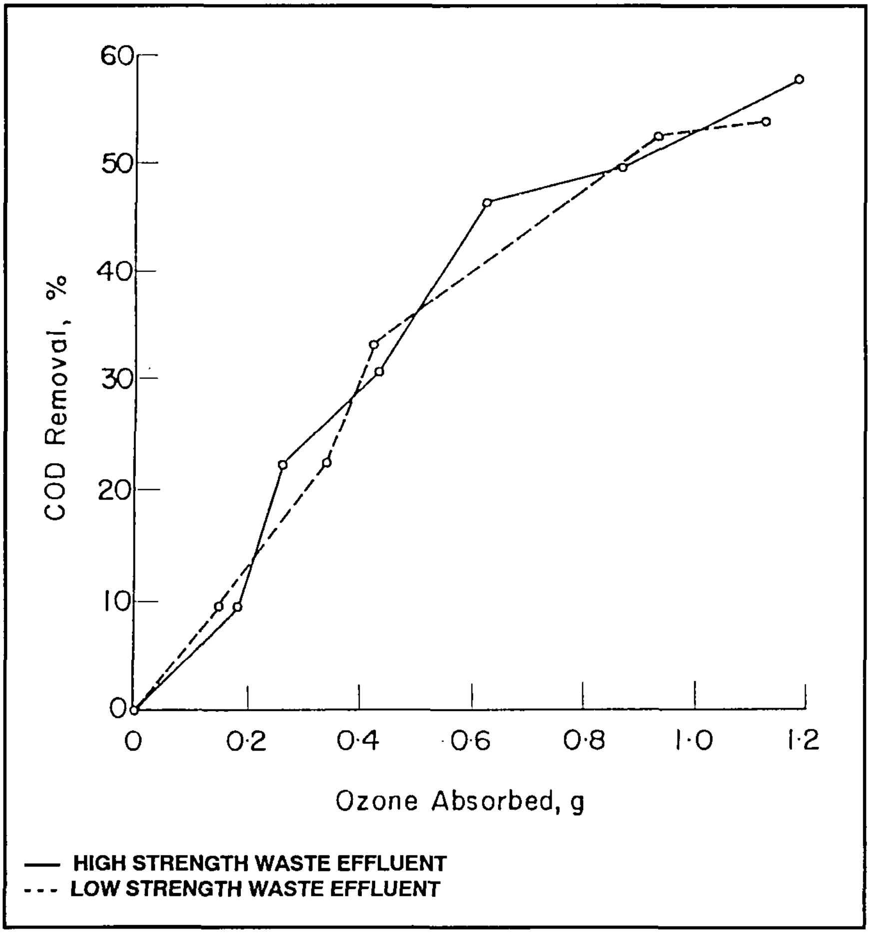


Figure 6. COD removal as a function of the amount of ozone absorbed..

brownish in color, leading to a slight JTU decrease. The reason for the visibility decrease after eight hours of ozonation is not known. It is presumably caused by some unknown small molecule intermediates. After that, the visibility steadily improves further.

Changes in pH and Suspended Solids

During ozonation, the pH and suspended solids (SS) concentration were also monitored. Typical pH and SS variations are displayed in Figure 9. It appears that there is little change in these two parameters during the ozonation period. Small change in SS is understandable because ozonation is a chemical decomposition

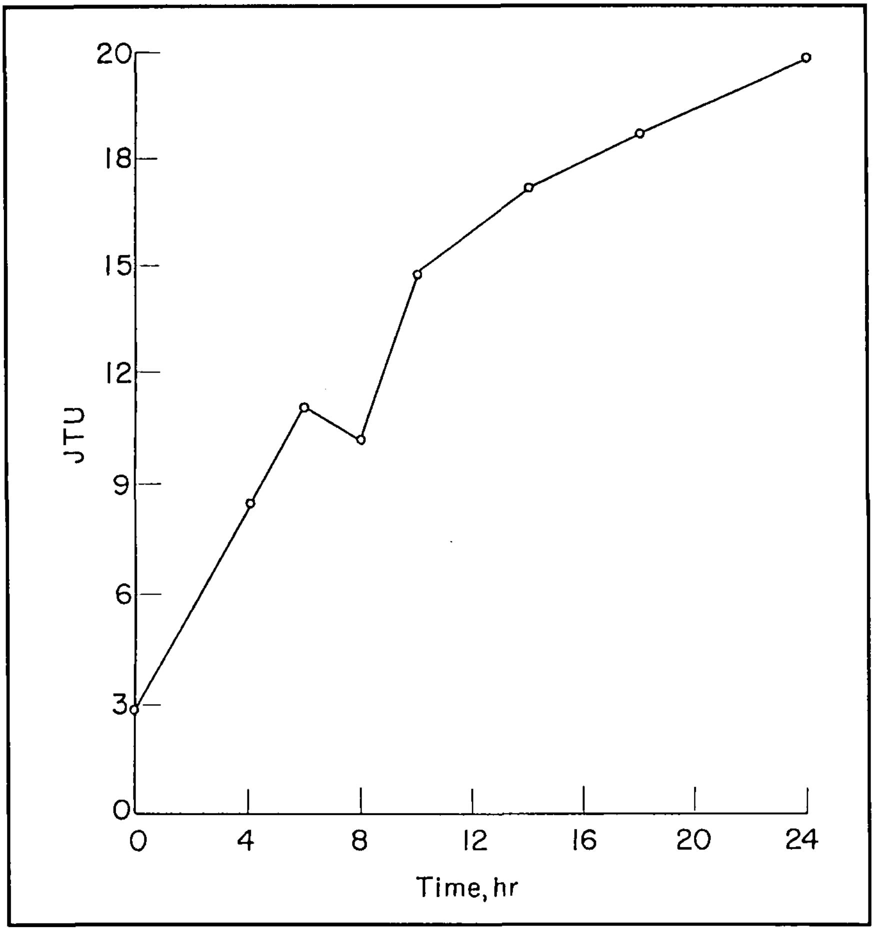


Figure 7. The JTU change of high strength textile waste effluent during ozonation.

process and no microorganisms are involved. This small SS change is particularly attractive because there will be no additional sludge to be disposed of; the sludge disposal of the conventional activated sludge process is usually a costly operation.

CONCLUSIONS

Experimental studies were conducted to investigate the efficiency of ozonation in removing the color or turbidity and the chemical oxygen demand of textile waste effluents. It has been found that under most circumstances, approximately six hours are sufficient to reduce the COD concentration of the textile waste

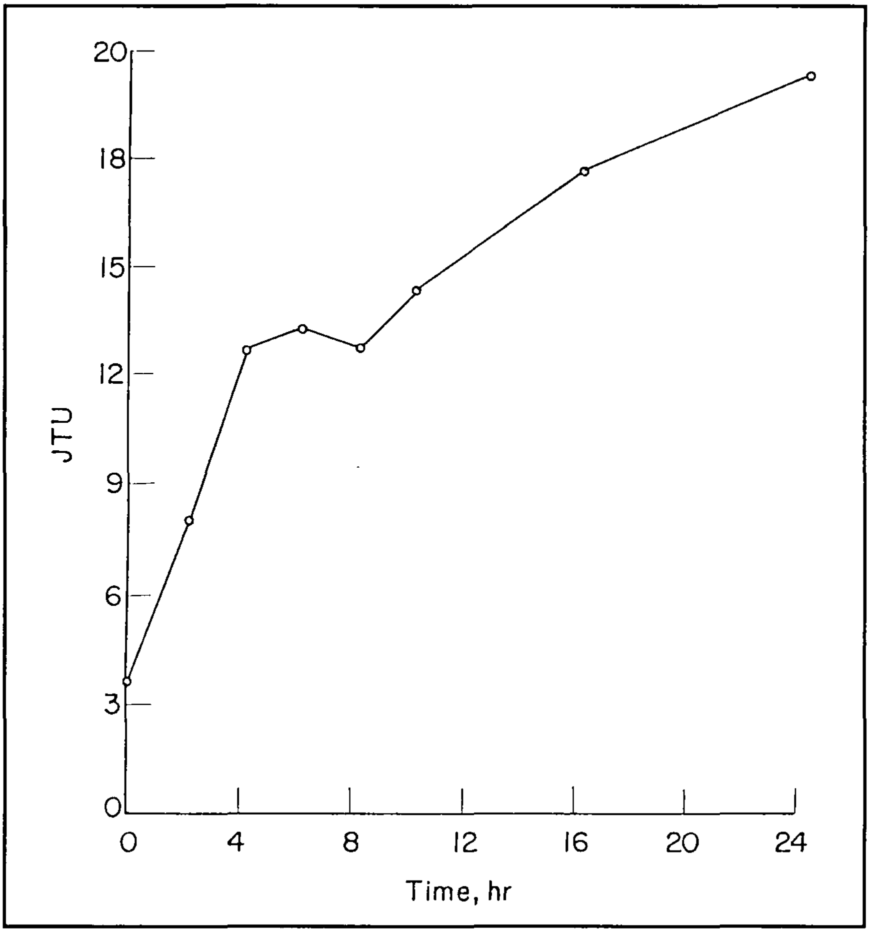


Figure 8. The JTU change of low strength textile waste effluent during ozonation.

effluent by one-half and to remove most of the color. The COD concentration cannot be further reduced because of formation of several small molecule organic compounds as the decomposition products of dyestuffs which are immune to ozonation. Those decomposition products of ozonation, however, can be fairly easily digested by an activated sludge process. Hence, ozonation in conjunction with the conventional activated sludge process could provide an effective means for dealing with the textile waste effluent.

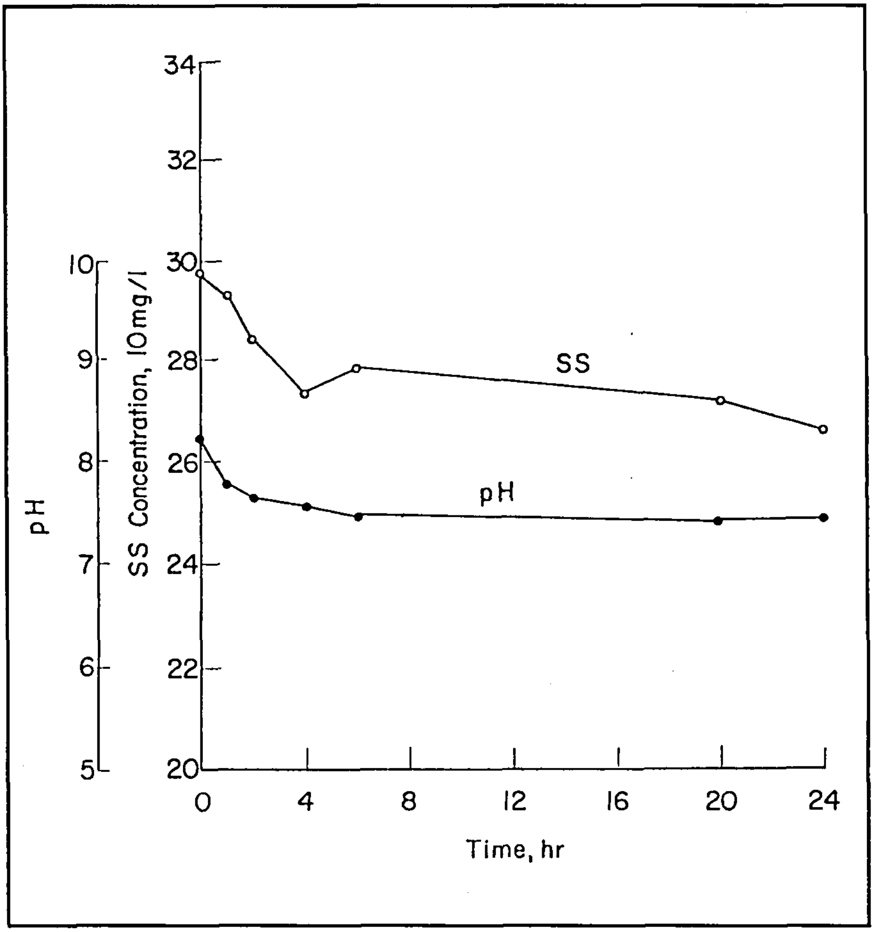


Figure 9. Variations of SS concentration and pH during ozonation.

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