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WASTEWATER TREATMENT BY COMBINED PROCESSES OF CHEMICAL OXIDATION AND MEMBRANE FILTRATION

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Abstract : This study is to investigate the effects of TOC removal by ozonation in the continuous membrane process after Fenton's treatment of textile wastewater. Experiments were conducted to examine the effects of various operating variables on the treatment efficiencies of the combined individual unit operations by ozonation and membrane separation. Ozonation was found to provide very efficient removal efficiency in the process, avoiding the exclusive ozone treatment. It was observed that the ozone-mediated membrane process acts not only as a sieving effects, but also as an oxidizer in promoting the removal efficiency of TOC. Present study in combined continuous process offers strong synergistic effects of the removal of color and TOC on the textile wastewater treatment. A prototype consisting of multiple steps of unit operations associated with ozone was proposed in this work, the proposed continuous hybrid-process including Fenton's oxidation, ozonation and filtration was shown to remove TOC very well to treat the textile wastewater.

Key Words : Fenton's oxidation, hybrid process, membrane, ozone, textile wastewater

INTRODUCTION

In the past several decades, wastewater discharges by dye manufacturing and dyeing/finishing plants have consistently been a major environmental concern. Those effluent discharges are notorious due primarily to their strong color, high dissolved solids and other organic substances. Those pollutants in the effluent discharges, if not removed, will cause upset to the ecological system of a receiving water body. Unfortunately, the dye-stuff, dyeing additives and sizing agents in the wastewater effluents are highly structured complex polymers, which are very difficult to decompose biologically. Hence, very little decomposition of those organic molecules takes place in a biological treatment process. Very often, strong color and turbidity of the wastewater effluents are particularly troublesome because of its negative visual impact. In industrial application, decolorization using hydrogen peroxide, sodium hypochlorite or various proprietary decoloring agents has been reported. However, polishing step using these decoloring chemicals is expensive. Search for more effective and less expensive methods in decolorization as well as pollutant reduction is in order.

Effective decolorization of dye wastewater by Fenton's oxidation was reported by Kang and Hwang,[1] Kuo[2] and Lin and Peng[3] considered dye decolorization by Fenton's reagent which is mixture of hydrogen peroxide and ferrous sulfate. The Fenton's reagent

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generates, in a sequence of chemical reactions, hydroxyl radical which is a very strong oxidant and accounts mainly for the decoloring reactions. In a more recent work, Davis et al.[4] utilized UV light in conjunction with semiconductor catalyst in investigating the kinetics of dye decolorization. As an alternative, ozonation had become a popular method researched by many researchers to remove effectively the color of the wastewater effluent.[5~8]

Although effective ozonation and Fenton's oxidation methods mentioned above do possess some inherent disadvantages, ozonation renders decomposition of highly structured dye molecules into smaller organic molecules. Although the color of the wastewater effluent was effectively removed by this method, there was a relatively small change in the chemical oxygen demand (COD) concentration of the treated wastewater primarily because of generation of small molecule organic compounds. Hence the treated wastewater very often still does not meet the discharge standard regulated by the government. In terms of COD removal, the membrane filtration is much improved method over ozonation. But the membrane can get easily saturated in the process, which requires regeneration of complete replacement. The membrane process hence can become quite expensive in practices. Combination of both methods into a single process could be often an attractive alternative to remedy the inherent disadvantages of ozonation, Fenton's oxidation and membrane filtration. The purpose of this work is to conduct experimental studies for the removal of TOC in the combined ozonation, Fenton's oxidation and membrane process to address this point. As will be shown later, the combined treatment process does offer considerable advantages unrealized by each of them.

MATERIALS AND METHODS

Experimental Apparatus

The experimental set-up consisted of a reactor which was 36 cm in ID and 100 cm long. The reactor, as shown in Figure 1, was equipped with external vessel to treat with Fenton's reagent. The wastewater treated by Fenton's oxidation was processed in the following reactor for ozone oxidation. At the bottom of the reactor, a solution sampling port and an ozone gas input port were provided. The ozone gas was generated by a PCI ozone generator (PCI, PA, USA) which was equipped with an air process unit (air compressor, air dehydrolyzer). The ozone generator was rated at 30 g/h as the maximum generation capacity. But the actual ozone output was primarily controlled by the inlet air flow rate as regulated by a rotameter to within 1 to 6 L/min in the present study. And the ferrous

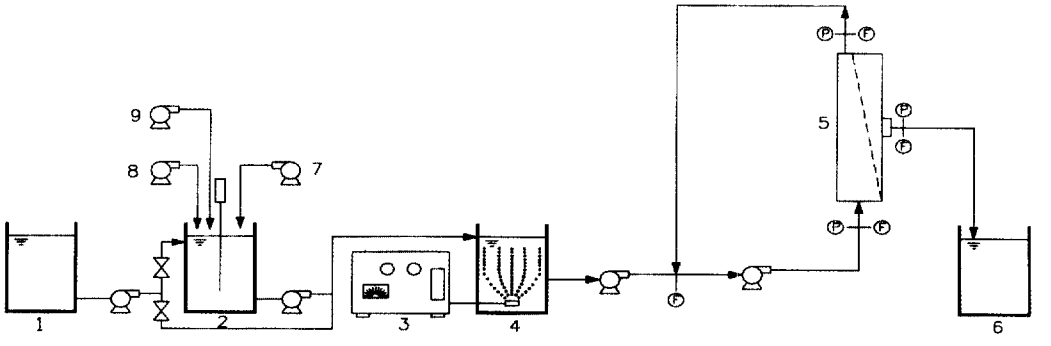


Figure 1. Schematic diagram of pilot plant (1: sedimentation reactor, 2: reaction tank by Fenton's reagent, 3: ozone generator, 4: ozone contactor, 5: UF membrane, 6: storage tank of treated water, 7: feed pump of ferric sulfate and hydrogen peroxide, 8: base pump for adjusting pH, 9: acid pump, mark 'P' inside circle: pressure gauge, mark 'F' inside circle: flowmeter).

Table 1. Detailed specifications of UF membrane

Material	Polysulfone
Operation press. (kg/cm^2)/Max. press.	2~3/7
Mambrane area (m^2)	5.0
M.W.C.O.	10,000
Filtration type	Crossflow hollow fiber

sulfate was obtained from Daejung Chemicals Co., Korea. UF membrane is a hollow fiber type of S Co., which is made of polysulfone and has 0.8 mm of ID, 1.4 mm of OD of hollow fiber and the overall dimension is ϕ 25 mm × 320 mm. Detailed specification of hollow fiber UF membrane was described in Table 1.

The raw textile wastewater used in the present study were obtained from a large dyeing and finishing plant in northern Gyung-kido area. The raw wastewater was first reacted using Fenton's reagent to remove suspended particles. During the experimental period, the water quality of the textile wastewater fluctuated significantly over a wide range. The color of the raw wastewater varied widely from time to time, reflecting the varying type of dyestuffs employed in the plant during the experimental period of the present study.

Methods and Analysis

Continuous experiments were adopted in the present study in order to facilitate identification of the optimum operating conditions of the combined treatment process. At the beginning of each test run, 60 L of raw textile wastewater was placed in the reactor for Fenton's oxidation. Ozone gas mixture at a desired flow rate between 1 and 6 L/min was immediately let in to start the experimental run in the ozone contactor. Small liquid samples were then taken periodically to determine the color absorbance and TOC concentration of the wastewater. The color degree was measured using HACH measuring device. The TOC concentration was measured by the TOC meter (5000A) of Shimadzu Co. In addition, the ozone concentrations in the ozone gas mixture entering and exiting the reator were determined using the UV detecting method using Wedco of PCI Co. Measurement of color was done using platinum-cobalt standard method provided HACH (Loveland, USA).

Reaction Mechanism of Fenton's Oxidation with Hydrogen Peroxide and Ozonation

Fenton's reagent is one of the best known metal catalyzed oxidation reactions of water-miscible organic compounds. It consists of ferrous salt such as $FeSO_4 \cdot 7H_2O$ and H_2O_2. This mixture results in Fe^{2+} catalytic decomposition of H_2O_2 and proceeds via a free radical chain process which produces hydroxyl radicals. The differences between H_2O_2 and Fe^{2+} for chemical substances should be attributed to the chemical nature of the pollutants. Unsaturated chemical compounds such as substituted phenols are more prone to oxidation by hydroxyl radicals because of their electron-rich double bonds. Oxidative destruction of dye-stuffs which contain only single bonds is accomplished solely through hydrogen abstraction which is more difficult with respect to kinetics. This may require higher concentrations for $OH\cdot$ which are generated by higher concentrations of Fe^{2+} and the question concerning the scavenging of $OH\cdot$ by Fe^{2+}, H_2O_2 and other $OH\cdot$ may arise.

The mechanism of Fenton chemistry can be described as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \quad (1)$$

$$OH\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O \quad (2)$$

Based on above chemical mechanism, the following reactions can be written as follows.

$$HO_2\cdot \rightarrow H^+ + O_2^-\cdot \quad (3)$$

$$O_2^-\cdot + Fe_3^+ \rightarrow Fe_2^+ + O_2 \quad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \quad (5)$$

$$Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^- \quad (6)$$

Walling[9] simplified the overall Fenton chemistry by taking consideration of dissociation water as follows:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad (7)$$

The ozonation is initiated by formation of hydroperoxide ion from the reaction between ozone molecules and hydroxyl ion in a solution and its mechanism is as follows.[10]

$$O_3 + OH^- \rightarrow HO_2\cdot + \cdot O_2^- \quad (8)$$

where

$$HO_2\cdot \Leftrightarrow \cdot O_2^- + H^+ \quad (9)$$

The hydroperoxide ion formed above reacts with ozone molecules to form hydroxyl free radicals.

$$O_3 + \cdot O_2^- \rightarrow O_3^-\cdot + O_2 \quad (10)$$

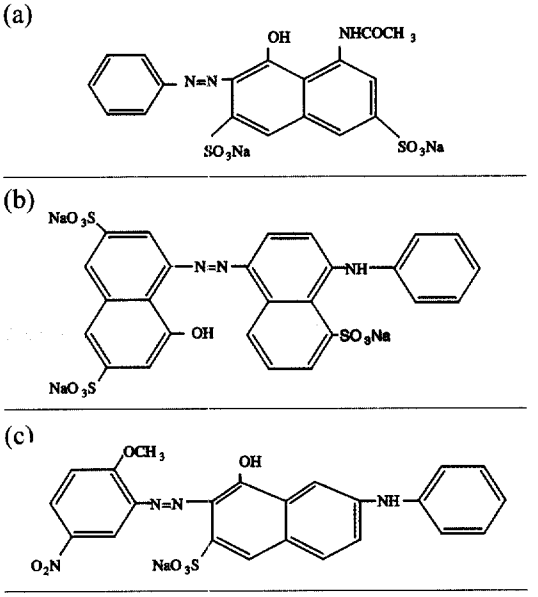
$$O_3^-\cdot + H_2O \rightarrow OH\cdot + OH^- + O_2 \quad (11)$$

RESULTS AND DISCUSSION

Chemical Compounds of Textile Wastewater

Textile wastewater has variable chemical compositions, for example, raw material such as anilines, intermediate products, and dye. The azo dyes used for present study are compounds containing azo groups (-N=N-) which are mainly bound to benzene or naphthalene rings and aromatic heterocycles in some cases. Intermediate products had following examples to manufacture products in the dye-finishing process: *p*-anisidine-iso-γ, 1-naphthalenol-8-sulfonic acid and 4-4'-nitroamino-diphenylamine-2-sulfonic acid. The azo dyes were Acid Red 1, Acid Blue 92, Acid Brown 2, Acid Brown 349, Direct Violet 51 and Direct Brown 116. Acid dyes were a large group of anionic dyes with a low molecular weight that carry 1 to 3 sulfonic groups, and they are mainly monoazo compounds. Representative chemical structure of azo dyes could be pictured as shown in Table 2.

Table 2. Chemical structures of dye in the textile wastewater, (a) Acid Red 1, (b) Acid Blue 92, (c) Acid Brown 2



During the experimental period, the water quality of the textile wastewater fluctuated significantly over a wide range. It had a pH between 5.1 and 9.2, a total organic carbon (TOC) concentration between 200 and 960 mg/L, a turbidity (NTU) between 50 and 510. The color of the raw wastewater varied widely from time to time and had a color PtCo unit between 70 and 200, reflecting the varying type of dyestuffs employed in the plant during the experimental period of the present study.

Optimal Condition of Fenton's Oxidation

Above equations of Equations (1)~(7) suggest that the presence of H^+ is required in the decomposition of H_2O_2, indicating the need for an acidic environment to produce the maximum amount of hydroxyl radicals.[9] In the presence of organic substances, excess ferrous ion, and at low pH, hydroxyl radicals can produce organic free radicals, these organic radicals may then be oxidized by Fe^{3+}, reduced by Fe^{2+}, and dimerized by a reaction mechanism shown in Equations (1)~(7). Therefore,

the removal efficiency of organic substances as shown in Figures 2 and 3 can be dependent upon by input amount of ferrous sulfate and hydrogen peroxide. Because this is due to the reactive hydroxyl radical generated in an acidic solution by the catalytic decomposition of hydrogen peroxide. In the presence of ferrous iron, the peroxide is split into $OH^-+OH\cdot$. Organic substrates are subject to free radical attack by the hydroxyl radical. This indicates that the organic substances cannot be effectively degraded in case of small input-amount of hydrogen peroxide, but in case of excess amount of hydrogen peroxide, the removal efficiencies of color and organic substances would be effective. In other words, unreactive hydrogen peroxide would make the TOC increase oppositively. Therefore, it is important to remove organic substances by appropriate amount of hydrogen peroxide and ferrous sulfate at optimal pH.

Optimal ratio of input ferrous sulfate : In an experimental test run, the raw wastewater placed in the reactor was 556 ppm of TOC. Hence, experiments were first carried out to test the effects of various amounts of $FeSO_4\cdot 7H_2O$ on the removal of TOC and color of wastewater at given set of other operating conditions such as input hydrogen peroxide of 29.5 mM/liter and pH 6.5. The test results were demonstrated in Figures 2~4. The effect of $FeSO_4\cdot 7H_2O$ on the TOC removal appears to be considerably more pronounced than that on the color removal as the input amount of ferrous sulfate increases from 1.8 mM/liter to 10.8 mM/liter. Figure 2 shows that the removal efficiencies of TOC were 47.1% and 80.9% in the input amount of 1.8 mM/liter and 3.6 mM/liter $FeSO_4\cdot 7H_2O$, respectively. But as the input amount of ferrous sulfate increases from 1.8 mM/liter to 44.1 mM/liter, the removal efficiencies of TOC were 80% or more. This indicates that there exists the optimal condition of the ferrous sulfate and hydrogen peroxide, that is, the mole ratio of $FeSO_4\cdot 7H_2O/H_2O_2$ is approximately 0.12.

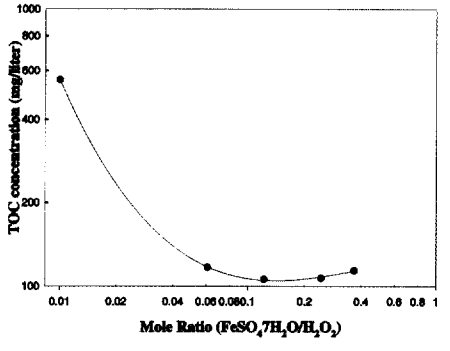


Figure 2. TOC variation in the concentration of 58.8 mM H_2O_2 and determination of optimal input concentration of ferrous sulfate.

Optimal ratio of input hydrogen peroxide : In experiment, the effect of hydrogen peroxide on the TOC removal was performed in the initial condition of TOC, 218 mg/L, as the input amount of hydrogen peroxide increased from 7.35 mM/liter to 117.6 mM/liter at given set of other operating conditions such as input ferrous sulfate of 1.8 mM/liter and pH 6.5. Figure 3 shows that the removal efficiencies of TOC were 29.6% and 57.3% in the H_2O_2 input amount of 7.35 mM/liter and 29.4 mM/liter, respectively. But as the input amount of hydrogen peroxide increased from 44.1 mM/liter to 117.6 mM/liter, the removal efficiencies of TOC were restricted and had a

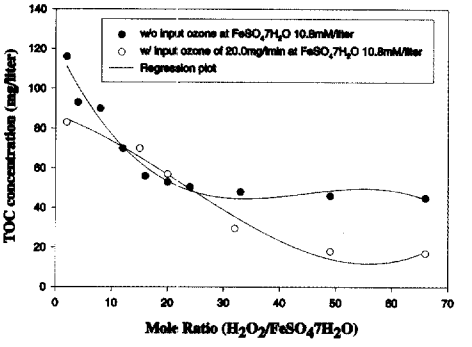


Figure 3. TOC variation in the concentration of 1.8 mM $FeSO_4\cdot 7H_2O$ and determination of optimal input concentration of hyrdrogen peroxide before/after ozonation.

limited value of 60%. This indicates that the rate of oxidation is dependent on the ratio of hydrogen peroxide to organic substance and the optimum ratio of the ferrous sulfate to peroxide exists. If excess of peroxide is present with a large amount of oxidizable material, this condition can be prevented by different operating conditions, for example, careful adjustment of $FeSO_4 \cdot 7H_2O$, H_2O_2, temperature, and pH etc.. The optimal condition in Figure 3 was appropriate when mole ratio of $H_2O_2/FeSO_4 \cdot 7H_2O$ was approximately 22. The difference of optimal condition between Figures 2 and 3 is seen to decrease considerably with an increase in the initial TOC concentration. For instance, for the wastewater with an initial TOC concentration of 218 mg/L, the TOC removal was high at 77.9%, but for that with an initial TOC concentration of 556 mg/L, the overall TOC removal was 73.0% at the optimal ratio of $H_2O_2/FeSO_4 \cdot 7H_2O$=22.

Optimal condition of reaction time : Figure 4(a) is to compare the effects of TOC removal with the reaction time after 5.4 mM/liter $FeSO_4 \cdot 7H_2O$ and 58.8 mM/liter H_2O_2 for the treatment of textile wastewater simultaneously put into the reactor as shown in Figure 1. As a result, the removal efficiency of TOC significantly increased by 34.1% after the reaction time passed 10 min and consistently reached 45.4% after the reaction time passed 20 min. But the removal efficiency became constant after 30 min of the reaction time and its value was over 50%. Therefore, appropriate reaction time would be 20~30 min when considering the economic points of view.

Optimal condition of reaction temperature : The reaction temperature in the continuous dye-finishing line was increased by 32℃ due to the heating of manufacturing line for dyeing and the heat consumption of pumping power. The effects of temperature in the course of Fenton's oxidation were significant, this observation confirms the results revealed by Figure 4(b). The results of Figure 4(b) clearly shows

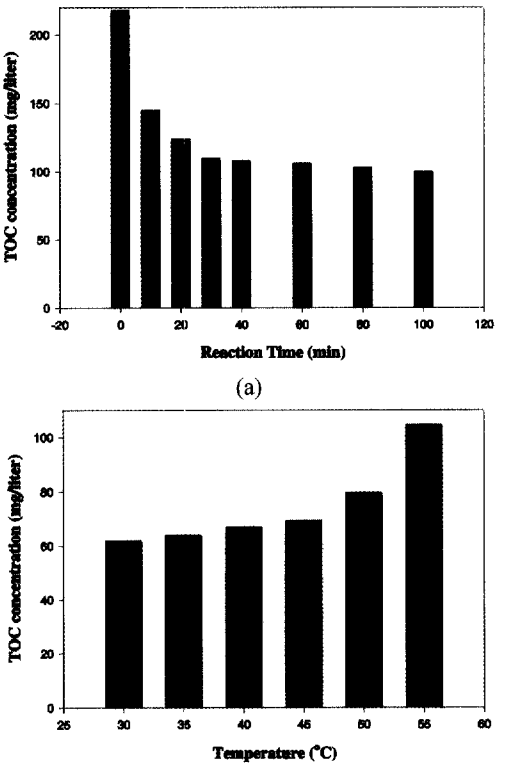


Figure 4. (a) TOC vs. reaction time under the fixed conditions of 5.4 mM/liter $FeSO_4 \cdot 7H_2O$ and 58.8 mM/liter H_2O_2, (b) TOC vs. reaction temperature under the fixed conditions of 10.8 mM/liter $FeSO_4 \cdot 7H_2O$ and 117.6 mM/liter H_2O_2.

that the reaction temperature plays a dominant role in the TOC removal of textile wastewater at pH 6.5 under the conditions of 10.8 mM/liter $FeSO_4 \cdot 7H_2O$ and 117.6 mM/liter H_2O_2 for the treatment and hence tests were run from 30℃ to 55℃ by an increase rate of temperature, 5℃. Temperature was highly beneficial to TOC removal and the removal efficiencies of TOC in the wastewater decreased 51.8% from 73% as a temperature increased from 30℃ to 55℃. Therefore, the reaction temperature for the Fenton's process was desirable to run less than 30℃, the removal efficiencies rapidly decreased at more than 50℃. This indicates that the rate of oxidation is highly exothermic and it is

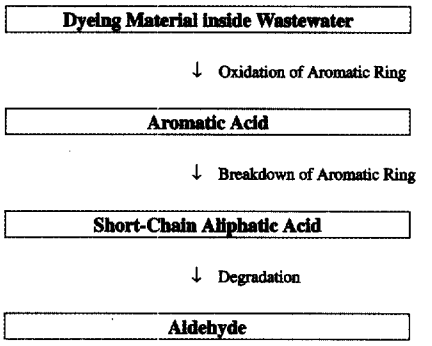
determined by the initial iron concentration and temperature and the reaction with Fenton's reagent is very sensitive to the temperature because the textile wastewater containing phenolic chemical compounds is highly reactive by the hydroxyl radical.

Effect of TOC and Color Removal by the Exclusive Treatment of Ozonation

The amount of ozone supplied by the PCI ozone generator could be conveniently controlled by the air flow rate at a fixed current input at 1.2 A. The effect of ozone on the wastewater about the removal of TOC was experimented to compare the exclusive treatment by ozonation with the treatment by ozonation after Fenton's oxidation.

The effects of ozonation in the textile wastewater were first performed through bypass valve without Fenton's treatment as shown in Figure 1. The dyestuffs in the textile wastewater used in the present study had structures with multiple rings and side chains as shown in Table 2. When the structural rings had double benzene rings or the side chains of natrium sulfate etc., they were severed by ozonation with following reaction mechanism of Equations (8)~(11). The mechanism of ozone reaction had an indirect path resulting from the decomposition of ozone to radicals, decomposition favored by basic pH in which the reaction was initiated by hydroxyl ions (OH^-) of Equation (8).[10] Many previous investigations[11,12] have shown that ozonation was highly effective in breaking down the straight, unsaturated bonds in the dye molecules, causing rapid decolorization of textile wastewater. However, the aromatic rings or side chains generated a large amount of small chemical molecules in the solution by the ozonation.[11] For example, the chemical compounds of wastewater listed in above section and shown in Table 2 had azo functional group, aromatic rings and naphtol sulfonic acid, they were oxidized and hydrolyzed due to the decyclization by ozone and produced aromatic acids

Table 3. Diagram of degradation of dyeing chemicals by ozone



such as muconic aldehyde and maleic acid. Such compounds are unstable and break down to short-chain aliphatic acid because ozone attacked conjugated double bonds. These sequential degradation mechanism was figured in Table 3. This phenomenon would be manifested by rapid color disappearance over 20%, but considerably less efficient TOC removal. These alteration of dyestuff molecules were then oxidized continuously to break down to the amine and carbon dioxide. After all, the organic substances of intermediate state might be more degradable and might generate small molecule organic compounds by the oxidation of an ozone during the long reaction time.

Figure 5 accounts for the highly effective color removal of ozonation, but considerably has less efficient TOC removal in present study. Hence, a color removal over 45% and a TOC removal of 21% could be achieved by ozonation which plays a dominant role in the color removal of textile wastewater. However, the organic or inorganic molecules generated during ozone decolorization could not be further decomposed to final products by ozonation alone. Therefore, the more advanced technique to obtain the removal efficiency of more than 50% is definitely needed.

Effect of TOC and Color Removal by Ozonation After the Fenton's Treatment

The removals of TOC and color by Fenton's oxidation was very drastic. For example, for

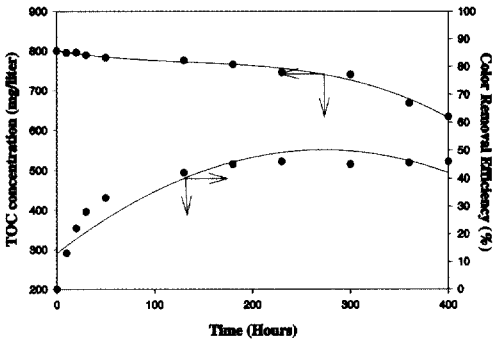


Figure 5. TOC variation and color removal efficiency by ozonation in the raw textile wastewater.

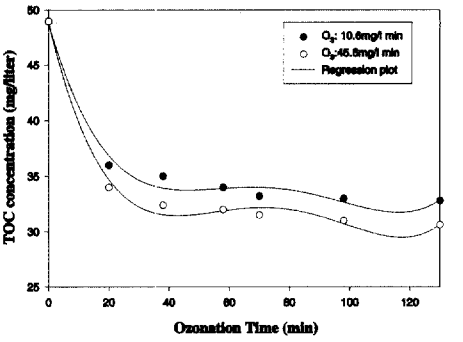


Figure 6. TOC removal effects by ozonation after Fenton's treatment.

the wastewater with an initial TOC concentration of 556.4 mg/L, the TOC removal was very high at 80.9% in the absence of ozone as shown in Figure 2. But the corresponding TOC removal by ozonation shown in the graph of Figure 5 without Fenton's process is quite low due to presence of a large number of various organic compounds. This indicates that the organic or inorganic molecules generated during ozonation could not be further decomposed to final products by ozonation alone as shown in Figure 5. This accounts for much little effect of ozone gas flow on the TOC removal.

Such a ozone-supported TOC removal after Fenton's treatment was considerably improved as shown in Figure 3. In terms of TOC removal, the treatment efficiency of textile wastewater was seen the effect of hydrogen peroxide on the TOC removal as the input amount of hydrogen peroxide increased from 7.35 mM/liter to 117.6 mM/liter at given set of other operating conditions such as input ferrous sulfate of 1.8 mM/liter and pH 6.5. Figure 3 shows that the removal efficiencies of color in the combined process of Fenton's oxidation and ozonation were overally 64.2% and 72.4% in the H_2O_2 input amount of 7.35 mM/liter and 29.4 mM/liter, respectively. But as the input amount of hydrogen peroxide increased from 44.1 mM/liter to 117.6 mM/liter, the removal efficiencies of TOC were restricted and had a constant value of 91.7%. This indicates that the ozonation of wastewater after the Fenton's treatment was dependent upon the ratio of hydrogen peroxide to ferrous sulfate and the combined process of individual unit operations of Fenton's oxidation and ozonation provided a better treatment efficiency of more than 10%.

It is shown in the graphs of Figure 6 to increase with an increase of the ozone concentration. For instance, for the wastewater with 49 mg/L concentration after a Fenton's treatment, the removal efficiency was approximately increased by 7% as the input ozone concentration increased from 10.6 mg/L·min to 45.6 mg/L·min for the same ozone gas flow rate. The ozonation plays a dominant role in the TOC removal of textile wastewater and hence an increase in ozone concentration is highly beneficial to TOC removal. To achieve an enhanced TOC removal, the ozonation after Fenton's treatment was more effective to remove TOC by 37% as shown in Figure 6. But the more advanced technique to obtain the removal efficiency of more than 99% is definitely needed.

The effect of ozone on the wastewater about the removal of color was compared between before and after Fenton's treatment as shown in Figure 7. The corresponding color removal by ozonation shown in the graph of Figure 5 without Fenton's treatment was quite low due to presence of a large number of various organic compounds. The color however can be effectively removed around 50% by Fenton's oxidation only, and such a ozone-supported color removal after Fenton's treatment was

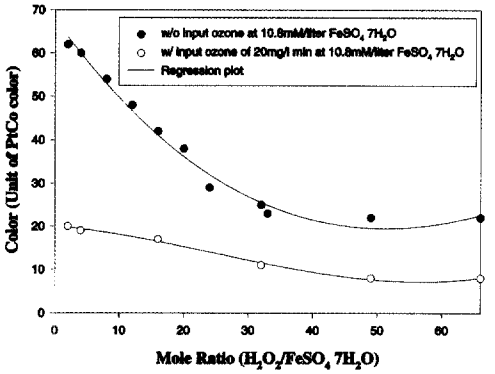


Figure 7. Color removal effects in the different molar ratio of $H_2O_2/FeSO_4 \cdot 7H_2O$ before/after ozonation.

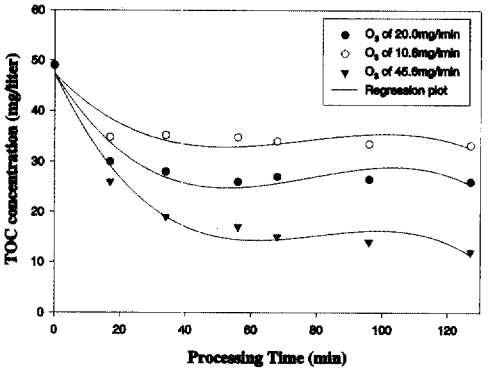


Figure 8. TOC removal effects by ozone-mediated membrane process.

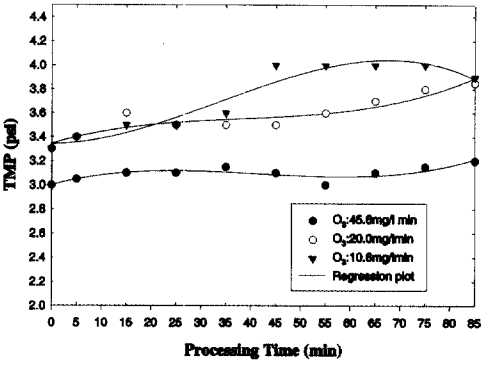


Figure 9. Flux effects in the different ozone concentrations of 45.6 mg/L·min and 10.6 mg/L·min.

increased from 60% to 85% as shown in Figure 7. This accounts for the highly effective color removal of ozonation, but considerably less effective in the removal of TOC. Hence even without membrane process, a color removal over 93% could be achieved by ozonation after Fenton's treatment.

Effect of TOC and Color Removal by UF Membrane After the Fenton's and the Ozone Treatment

The primary role played by membrane process in the wastewater treatment application is a separation of solute by micro-filtration. Three test runs were performed for comparison to evaluate the effect of ozone in the membrane process of the present system. Three tests were conducted in the reactor that 10.6 mg/L·min, 20.0 mg/L·min and 45.6 mg/L·min of input ozone were spared into the ozone contactor. The input ozone was added to 60 L wastewater in the contactor with the content being kept well mixed by a stirring baffles. The test results of these two runs are compared in Figure 8 to confirm this ozone-mediated membrane process in the treatment. The membrane operation mediated by ozone was conducted to remove the organic substances and to enhance the permeate flux in the process. Figure 9 shows that the TMP (trans-membrane pressure) decreased about 25% as the input amount of ozone increased from 10.6 mg/L·min to 45.6 mg/L·min.

After chemicals in the wastewater were severed by ozonation as manifested by rapid color disappearance over 60% after Fenton's treatment, the organic substances of textile wastewater became more degradable and generated small molecule organic compounds. This generation could be conformed by UV_{254}, which indirectly measures the numbers of molecules in the wastewater.[13] The increase of UV_{254} does come until after 15 min of treatment as shown in Figure 10. This implies that within the first 5 min, ozonation was the major mechanism of molecular alteration. As time passes, the organic substances inside wastewater were degraded and the number of degraded small organic substances had a maximum point at 15 min and then has a constant value of UV_{254}, which organic sub-

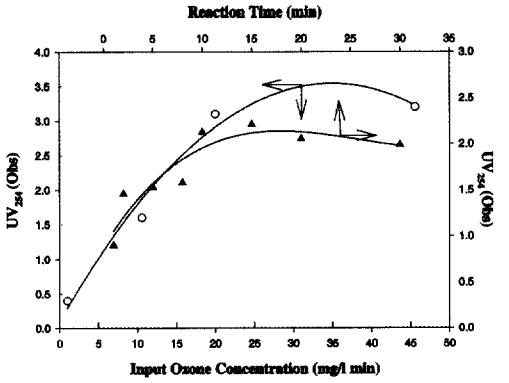


Figure 10. UV_{254} effects of textile wastewater by ozonation variables, for instance, reaction time and input ozone concentration at the reaction time of 8 min.

stances indicates to be dimerized for pollutant removal after 20 min. As noted earlier, dyestuff molecules could generate more organic molecules in the wastewater. The organic molecules decomposed by ozone regardless of the structures of dyestuffs or altered ones made the filtration in the porous membrane easy, this indicates the decrease of TMP in the membrane as shown in Figure 9. Lots of data of the permeate flux by ozonation in the membrane filtration was described in detail by Park.[14)]

The variation of UV_{254} is also strongly dependent upon the ozone concentration. For example, in case of input ozone of 47 mg/L·min, a value of UV_{254} is higher in comparisons with those of 10.6 and 20.0 mg/L·min. This is because there is significantly more dissolved ozone and a reaction time with different ozone concentration available in the wastewater on the per unit TOC weight basis in comparison with that with high initial TOC concentration. If more ozone concentration is provided, the shorter reaction time with organic chemicals is needed.

From above results, both ozonation and membrane process are equally important in removing wastewater TOC concentration. Furthermore, the membrane process might get a good result to remove TOC. The test results of these three runs were compared in Figures 8 and 9 for the membrane process. But the TMP became essentially constant in 90 min because chemicals were fully saturated after that time in the ozone treated water. And for the case with combined ozonation and membrane filtration, there was a steady increase in the TOC removal with time even after 60 min of treatment. Above figures show that the change in the TOC concentration affects the treatment of combined ozonation, Fenton's oxidation and membrane process. It is obvious that in terms of TOC removal, the treatment efficiency of textile wastewater was seen in the graphs to decrease considerably with subsequent processes in the TOC concentration. For instance, for the wastewater with an initial TOC concentration of 218 mg/L, the TOC removal was high at 80.9% for the Fenton's process, but for that with ozone process, the overall TOC removal was drastically reduced by 93.8%. This is due to the fact that the removal efficiency is dependent upon the amount of ozone available in the wastewater for the same ozone gas flow rate. Hence, for high ozone concentration in comparison of the amount of ozone consumed per unit weight of TOC removal, ozone is more efficiently utilized for wastewater in the membrane process as shown in Figure 8.

The corresponding TOC removal by ozone-mediated membrane as shown in the Figure 8 shows that those chemical compounds could be removed and considerably improved as the input amount of ozone increased. The most significant improvement in the TOC removal appeared to occur in high ozone concentration. In fact, it was observed in all experimental runs at 4 L/min of ozone gas flow and with 10.8 mM/liter $FeSO_4 \cdot 7H_2O$. The removal efficiencies of TOC in the membrane process was overally 93.8% in case of the wastewater treated by 10.6 mg/L·min of input ozone as shown in Figure 8. But the removal efficiencies of TOC were increased by 95.1% and 98.5% in case of 20.0 mg/L·min and 45.6 mg/L·min of input ozone.

The higher removal efficiency in the mem-

brane process in comparison with Fenton's oxidation/ozonation would be speculated that better removal efficiency of TOC might occur in due to the adsorptive-seiving effect by higher ozone concentration in the porous polysulfonic anion-membrane.

CONCLUSIONS

Experiments were conducted to investigate the treatment of textile wastewater by continuous individual processes including the Fenton's process, the ozone-contacted process and the membrane process. Emphases were placed on examining the performances characteristics of the combined treatment process. Results from all experimental runs revealed that:

1. Addition of membrane process did little improvement of color removal over that by ozonation. In fact, the removal efficiency of color can be achieved over 93%.
2. An increase of ozone concentration after Fenton's treatment was found to improve the TOC removal efficiency of 10%.
3. In the beginning of a treatment run, chemical components in the wastewater started to oxidize organic molecules by Fenton's reagents, and ozonation played an important roles to remove chemicals between 5 and 20 min after Fenton's treatment. After 20 min, an ozonation degraded chemicals in the wastewater into small molecules.
4. Based on overall process using Fenton's oxidation/ozonation/membrane filtration mechanism, the TOC treatment efficiency of textile wastewater got a good result of almost 99%.

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