

폴리설펜 한외여과막공정에서 오존의 영향

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Effect of Ozonation on Cross-flow Filtration of Polysulfone Ultrafiltration Membrane

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요약 : 폴리설펜 한외여과막 분리막공정을 이용하여 투과유속 상에서의 오존의 효과를 고찰하였다. 처음에는 조제한 페놀용액을 이용해 오존의 농도 10-45 mg/l·min을 가한 후에 분리막내에 막오염 제거를 목적으로 시도하였으며 이후에는 오존과 분리막이 혼합된 연속공정에서 폐수처리를 위해 오존에 의한 동일효과를 고찰하기 위해 시도하였다. 전처리 방법으로는 펜톤 산화법을 이용하여 화학응집을 시도하였고 그 결과 폐수내 용존유기물 제거에 효과가 있는 것으로 나타났다. 실험결과 오존을 이용하게 되면 투과유속이 10% 이상 증가한다는 사실이 조제수와 폐수에 공히 같게 나타났으며 오존과 과산화수소를 이용한 고도처리에서도 투과유속증가에 더욱 효과적이었다. 특히 오존을 이용한 처리수에서는 투과압력이 12% 이상 낮아지는 효과가 나타났으며 분리막 공정에 오존처리는 막오염을 거의 제거하기보다는 막오염을 제한적으로 막는 효과를 얻었다.

Abstract : Effect of ozonation on permeate flux was studied by using polysulfone ultrafiltration membrane. The filtration was first carried out by permeating phenol solutions under 3 kg/cm² until steady-state flux was obtained. Then, the ozone of concentration range between 10 and 45 mg/l·min was ozonated in water for reducing the fouling on the UF membrane. Treatment of chemical wastewater by combined ozone and membrane filtration methods was also investigated for the final purpose. The Fenton method assisted by chemical coagulation was employed as a pretreatment method and found to be highly efficient in removing a large amount of organic compounds. And it was found that the ozonation made the permeate flux enhance in the phenol solution and phenolic-chemical wastewater by 10% and oxidation by ozone and hydrogen peroxide was more effective. Evidence was presented that TMP decreased in more ozone concentrated water and it was found that the ozone-mediated membrane would have a limited role to prevent the membrane fouling rather than to eliminate fully.

Keywords : ozonation, cross-flow filtration, ultrafiltration

1. Introduction

The most important disadvantage of membrane

filtration is the declination of permeate flux due to membrane fouling, resulting from gel layer formation on the membrane surface, adsorption of solute on the membrane pores and blocking of pores by rejected solutes. Serious problems in

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performing efficient membrane operation are encountered in both microfiltration and ultrafiltration. For two decades, this problem has attracted much attention and a number of ways have been available for reducing the extent of fouling. To control fouling and concentration polarization, improvement methods of membrane performance are classified into four categories: pretreatment of feed solution, adjustment of membrane material properties, membrane cleaning and improvement by operating condition. Practically, what is most widely used in membrane separation process is the cleaning technique by hydraulic, mechanical, chemical and electrical methods. The hydraulic cleaning including back-washing is the most important method for reducing membrane fouling. However, this technique interrupts the continuous filtration process and cannot maintain the membrane operating at high permeate flux. More recently, electric cleaning technique was developed, which was applied by using pulsed electric field to membrane filtration. As a result, the charged particles fouled on membrane were removed away from the membrane [1].

The ozonation effect has been few studied for the enhancement of permeate flux in the membrane process. First of all, the use of ozone-mediated membrane in the drinking water system has been utilized as an alternative method of prechlorination which should be avoided in order to reduce THMs in tap water. The purpose of ozone-use is to prevent the membrane fouling in the process and to prolong the life-expectancy of membrane as well as to enhance the water quality. In this study, the ozonation was integrated to the membrane process and studied the factors affecting an increase of permeated flux.

The objective of this investigation is first to explore the feasibility of using the ozone-mediated membrane filtration method to reduce the membrane fouling using phenol solution as a fundamental work. Membrane filtration by the chemical oxidation was secondly tried in the chemical wastewater containing phenolic chemicals after pretreatment by chemical coagulation of Fenton's oxidation. Combination of both methods into a single process could often an attractive alternative to remedy the inherent disadvantages of ozonation and membrane

filtration. The purpose of this work is to conduct experimental studies of 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.

2. Theory of chemical oxidation

2.1. Pressure drop in the hollow-fiber UF system

The well-known Hagen-Poiseuille law for laminar flow through pores is used to express the average pressure drop across the membrane surface, P_m :

$$\Delta p_m = \frac{8\mu\Delta x Q_p}{r_p^2 \epsilon A} \quad (1)$$

in which x is the thickness of the membrane layer, μ is the fluid viscosity, Q_p is the total permeate flow through the pores, r_p is the radius of one membrane pore, ϵ is the porosity of the membrane, and A is the surface area of the membrane.

Because the thickness of the membrane, porosity, and pore radius in Eq. (1) are difficult to measure directly, they are collectively defined as the inherent resistance of the membrane, R_m :

$$R_m = \frac{8\Delta x}{r_p^2 \epsilon} \quad (2)$$

The unit of R_m is m^{-1} . Substituting Eq. (2) into Eq. (1) results in

$$\Delta P_m = \frac{\mu R_m Q_p}{A} \quad (3)$$

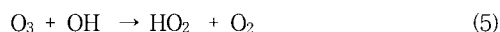
The definition of transmembrane pressure (TMP) across the hollow-fiber membranes may be used to express P_i in terms of permeate and retentate flows. Assuming a linear decrease in pressure along the membrane fibers, the transmembrane pressure can be expressed in terms of average pressure drop along the membrane fiber [2]:

$$\Delta P_m = \frac{P_i + P_o}{2} = \frac{\mu R_m Q_p}{A} \quad (4)$$

P_b is the change in pressure across the backpressure as shown in Fig. 2. The bypass pressure (P_s) of Fig.2 can work for controlling the flow rate and it was not used for present study.

2.2. Reaction mechanism of ozone's oxidation with hydrogen peroxide

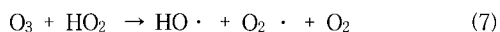
The reaction is initiated by formation of hydroperoxide ion from the reaction between ozone molecules and hydroxyl ion in a solution in the presence of hydrogen peroxide.



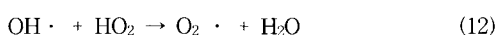
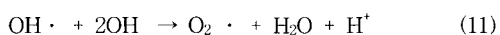
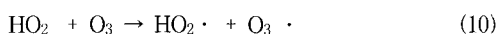
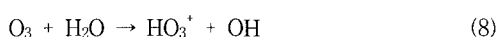
Since hydrogen peroxide is a weak acid, its partial dissociation in water produces additional hydroperoxide ions



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



Following the above step, a series of chain reactions involving the hydroxyl radical, superoxide, and ozonide ions occur [3].

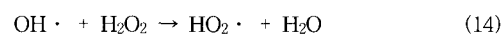


2.3. Reaction mechanism of Fenton's oxidation with hydrogen peroxide

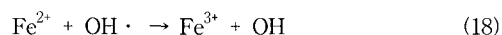
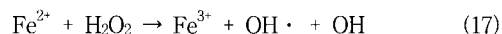
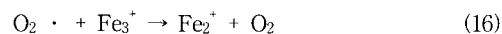
Fenton's reagent is one of the best known metal catalyzed oxidation reactions of water-miscible organic compounds. It consists of ferrous salt such as $FeSO_4 \cdot 7H_2O$ and H_2O_2 . This mixture

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 phenolic compounds 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 which are generated by higher concentrations of Fe^{2+} and the question concerning the scavenging of OH by Fe^{2+} , H_2O_2 and other OH may arise.

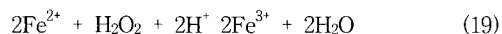
The mechanism of Fenton chemistry can be described as follows:



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



Walling [4] simplified the overall Fenton chemistry by taking consideration of dissociation water as follows:



3. Materials and Method

3.1. Membrane

Fig. 1 illustrates schematic of the experimental apparatus. A module of hollow fiber membrane, having a nominal pore size of $0.1 \mu m$, a surface

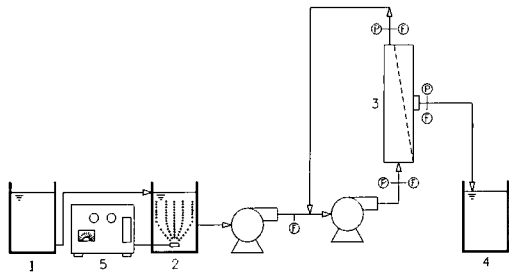


Fig. 1. Schematic diagram of pilot plant
 1) raw water (Fenton's oxidation) 2) ozone contactor, 3) UF membrane module 4) permeate storage tank 5) ozone generator
 P: pressure gauge, F: flow meter.

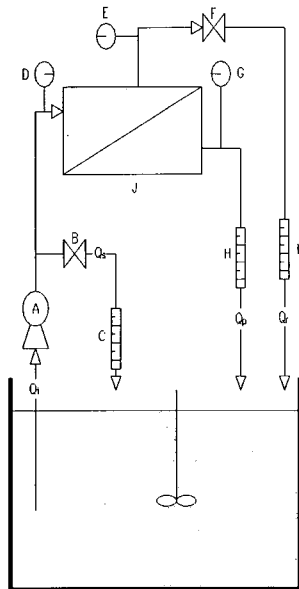


Fig. 2. Schematic of hollow-fiber UF system
 A: feed pump, B: bypass valve, C: bypass flow meter, D: inlet pressure transducer, E: retentate pressure transducer, F: backpressure valve, G: permeate pressure transducer, H: permeate flowmeter, I: retentate flowmeter, J: UF hollow-fiber membrane, Q_t : total volume rate, Q_p : permeate volume rate, Q_r : retentate volume rate.

area of 0.5 m^2 and a polysulfone material, was installed in an acrylic housing. Hollow fiber has 0.8 mm of ID, 1.4 mm of OD and separation capacity is 10,000 MWCO, the overall dimension is $25 \text{ mm} \times 320 \text{ mm}$. Synthetic phenol solution, which was made into 0.5 M concentration by

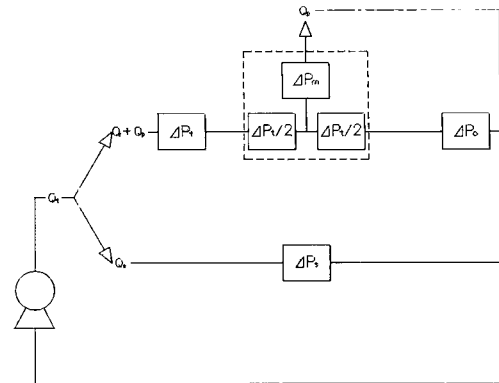


Fig. 3. Hydraulic components of hollow-fiber UF system
 subscript t: total, subscript p: permeate, subscript r: retentate, subscript s: bypass, subscript m: membrane surface, subscript o: backpressure.

suspending phenol in distilled water, was pumped into the membrane-housing without any pretreatment, and the excess amount of raw water was bypassed back into the mixing tank. Thus the membrane-housing was pressurized to give a driving force to the filtration. TMP was measured at the front of membrane module and during the filtration as shown in Fig. 2 and filtration was continued for several hours. Fig. 3 shows the hydraulic components of hollow-fiber UF system of Fig. 2. Consequently, the filtration was performed after the ozonation, the raw water is further treated in the membrane process, elevating the water quality of the final effluent to a standard for safe discharge.

The raw chemical wastewater applied in the present study were also obtained from a large dyeing and finishing plant in northern Gyungkido area. The raw wastewater was first reacted using Fenton's reagent to remove suspended particles as a pretreatment method. During the experimental period, the water quality of 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 560 mg/l, a turbidity (NTU) between 50 and 210. 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.

As schematically illustrated in Fig. 1, the ozonation on UF was studied by using experimental setup of cross-flow filtration pressure-units that was made of acrylic tube. Three experimental runs were carried out to verify the effectiveness of ozonation on TMP in order to investigate the effect of ozonation on preventing membrane fouling.

3.2. Experimental apparatus

After the ozone-Fenton's oxidation, the wastewater is further treated in the membrane process, elevating the water quality of the final effluent of wastewater to a standard for safe discharge or even for reuse as non-portable water. Such a combined chemical oxidation and membrane treatment was found to be highly efficient and may offer an advantages in dealing with the high variability of pollutant content in the chemical wastewater. The experimental apparatus of the present investigation consisted of three major parts: chemical coagulation by Fenton's oxidation, ozone oxidation and membrane process unit as shown in Fig. 2. The three treatment units could be operated independently in a batchwise fashion or in combined sequence.

The batchwise mode was adopted for determining the individual operating conditions. In a combined sequential treatment test run, the wastewater was first fed to the chemical coagulation tank for pretreatment. The effluent from that unit was then oxidized in the set-up consisted of a ozone contactor which was 360 mm in ID and 1,000 mm long. 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. Finally the wastewater effluent was fed to the membrane process unit.

In the chemical pretreatment, the reactor, as shown in Fig. 1, was equipped with external vessel to treat with Fenton's reagent consisted of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 . The ferrous sulfate was obtained from Daejung chemicals co., Korea and the hydrogen peroxide was done from Junsei chemicals co., Japan.

In each test, a desired amount of hydrogen peroxide chosen between 10 ml and 100 ml was added to the contactor before the ozone generator was turned on. The Fenton oxidation for chemical coagulation lasted usually less than 30 min. The samples were then taken for water quality measurements. It is noted that during the Fenton treatment of the wastewater, a certain amount of ferrous sulfate was continuously dissolved into the wastewater. In the wastewater, the dissolved iron in conjunction with the externally added hydrogen peroxide functions and thus the synergistic effects of the membrane process and the ozone oxidation will be elaborated later.

3.3. Methods and analysis

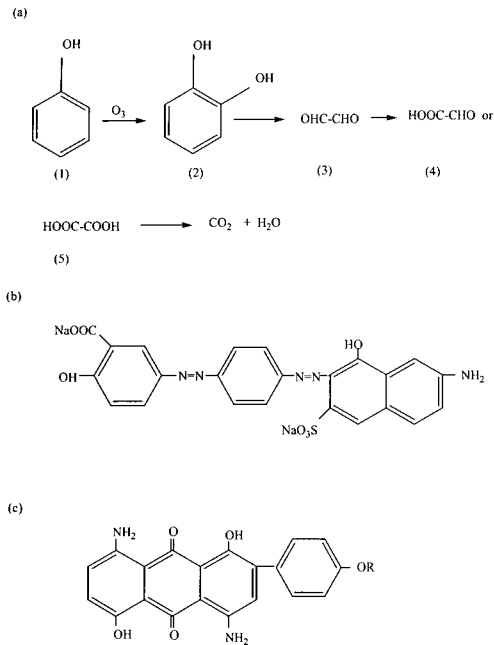
Batch experiments were adopted in the present study in order to facilitate identification of the optimum operating conditions of the combined treatment process. Small liquid samples were then taken periodically to determine the color absorbance and TOC concentration of the wastewater. The color degree 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 reactor were determined using the UV detecting method using Wedeco of PCI Co..

4. Results and Discussion

4.1. Effects of ozone in the hollow fiber membrane process (in case of phenol solution)

Three test runs were performed for comparison to evaluate the effect of ozone in the membrane process of present system. These tests were

Table 1. Chemical reaction mechanism and chemical structures of wastewater



- a) chemical reaction mechanism of ozone and phenol
 1) Phenol, 2) Catechol, 3) Glyoxal,
 4) Glyoxylic acid, 5) Oxalic acid
- b) Chemical structure of Benzidine polyazo-dye C.I. Brown 2
- c) Chemical structure of Bromamine acid anthraquinon-dye C.I. Disperse Blue 73

conducted in the reactor that the concentration ranges of input ozone between 10.6 mg/l · min and 45.6 mg/l · min were spared into the reactor. The input ozone was added to the reactor of 20 liter with the content being well-mixed by a stirring baffles. The test results of these runs were compared in Fig. 4~Fig. 8 to confirm this ozone-mediated membrane process in the treatment. The membrane operation mediated by ozone was conducted to remove the membrane-fouling and to enhance the permeate flux in the process.

The mechanism of membrane fouling and factors affecting membrane fouling are widely discussed. But no conclusive explanation has proposed due partly to the complexity of membrane-fouling. Colloids and inorganic salts as well as organic substances like humic acid are cited to

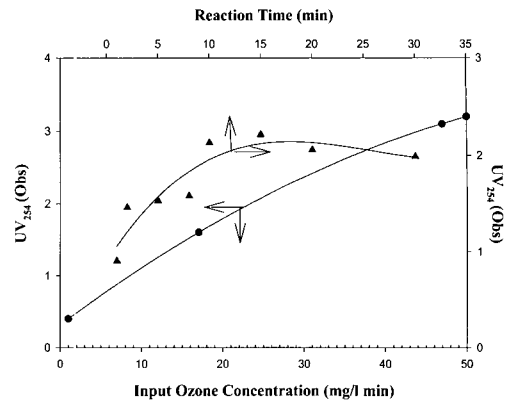


Fig. 4. Variation of UV₂₅₄ in the phenol solution by ozonation variables, for instance, input ozone concentration and reaction time in case of input ozone concentration of 45.6 mg/l · min.

cause membrane fouling in portable water treatment. Ozone is one of the strongest oxidizer on the earth, and can oxidize both organic and inorganic constituents. Since phenol solution used in this study is organic, organic fouling materials will be oxidized by an ozone. The working mechanism on fouling prevention can hardly explained by oxidation of organic fouling constituents. But the phenol used in the present study had structures with benzene ring and side chain. When the structural ring like phenol has a benzen ring or the side chain, they were severed by ozonation and reacted by the chemical reaction mechanism as shown in Table 1(a): Phenol→Catecho.→Glyoxal→Glyoxylic acid→Oxalic acid→Carbon dioxide. Many previous investigations have shown that the ozonation was highly effective in breaking down the straight, unsaturated bonds in the chemicals. However, the ring opening or side chain generated a large amount of small chemical molecules in the solution by ozonation. This accounts for the highly effective color removal of ozonation, but considerably less efficient phenol removal. And then, the organic substances were more degradable and generated small molecule organic compounds by the oxidation of an ozone. This generation could be explained by UV₂₅₄, which indirectly measures the numbers of molecules in the wastewater [5].

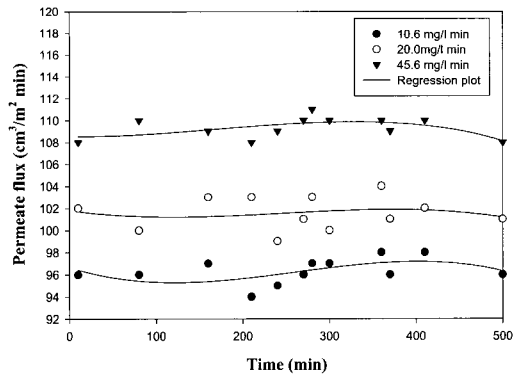


Fig. 5. Effect of permeate flux in the different ozone concentrations of between 10.6 mg/l·min and 45.6 mg/l·min in the phenol solution.

The increase of UV_{254} does come until after 15 min of treatment as shown in Fig. 4. This implies that within the first 5 min, ozonation might be the major mechanism of molecular alteration. As time passes, the organic substances inside wastewater were degraded more 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 substance dimerized for pollutant removal after 20 min. Therefore, this indicates that the number of degraded small organic substances was strongly dependent upon the ozone concentration. For example, in case of input ozone of 47 mg/l·min, a value of UV_{254} had the highest value. This implies that the chemicals were degraded by more dissolved ozone available in the solution on the per unit phenol weight basis in comparison with that with high initial phenol concentration.

As a result, the phenol solution was firstly utilized to test the possibility to enhance the permeate flux by the input ozone concentration. Fig. 5 shows that the flux rate increased about 12% as the input amount of ozone increased from 10.6 mg/l·min to 45.6 mg/l·min. The filtrated effluent increased as the input ozone concentration increased.

Fig. 6 shows the results of trans-membrane pressure (TMP) in input ozone concentrations of 10.6 mg/l·min and 20.0 mg/l·min in comparison with those of 45.6 mg/l·min. TMP in case of

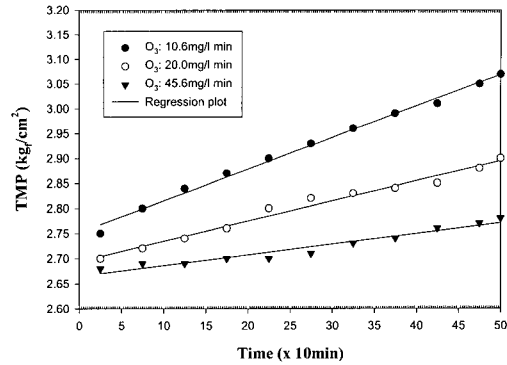


Fig. 6. Effect of TMP in the different ozone concentrations of between 10.6 mg/l·min and 45.6 mg/l·min in the phenol solution.

input ozone of 10.6 mg/l·min reached to 3.0 kg/cm², the slope of a linear line in relation with processing time was 6.342×10^{-4} in case of input ozone of 10.6 mg/l·min in comparison with the slope of 2.11×10^{-4} in case of input ozone of 45.6 mg/l·min and TMP decreased by 12% as shown in Fig. 6. It is obvious that more ozonation was effective to subdue membrane fouling due to less requirement of TMP. As a result, the slope proportionally increased 2.11×10^{-4} , 4.01×10^{-4} , 6.34×10^{-4} as the ozone concentrations decreased from 45.6 mg/l·min, 20.0 mg/l·min to 10.6 mg/l·min, respectively. Therefore, TMP continued to rise, indicating that ozone-dispersing before membrane processing was relatively effective to prevent membrane fouling once the fouling-material was degraded before attaching to the membrane.

Fig. 7 shows that the higher ozone concentration was, the lower rejection rate occurred. The rejection rate was proportionally decreased as the input ozone concentration increased by 10 mg/l·min. This was related to the degradation of chemicals by the oxidation of ozone and might prolong the life expectancy of membrane as overcoming flux decline of membrane.

In system using both molecular ozone and OH oxidation, the overall degradation rate of pollutant was relatively fast due to the hydroxyl, superoxide radicals made by Eqs. (7)~(12) with molar ratio of H_2O_2/O_3 until an optimum ratio was reached and they have a synergistic effect in the Fenton's

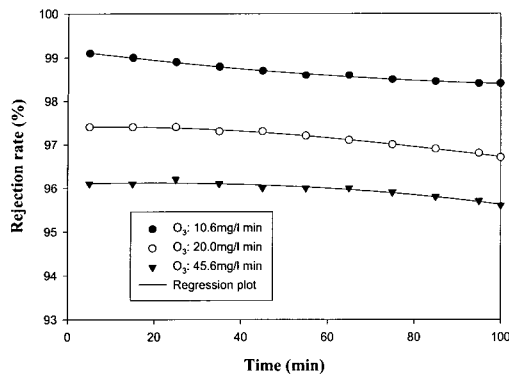


Fig. 7. Effect of rejection rate in the different ozone concentrations of between 10.6 mg/l·min and 45.6 mg/l·min in the phenol solution.

process by the radical reactions of $O_2 \cdot$, O_3 , $OH \cdot$. When the hydrogen peroxide was added in an excess, a strong acceleration of decomposition of O_3 by H_2O_2 at pH values above 5 occurs. The free radicals of Eq. (7)~(12) produced by a reaction of O_3 with an ionized form of hydrogen peroxide made the decomposition effect of organic substance increase. Staehelin *et al.* [6] reported that the rate constant for decomposition of O_3 initiated only by its reaction with OH was $210 M^{-1}s^{-1}$, but the rate constant with O_3 when present as the anion, HO_2^- , was $5.5 \times 10^6 M^{-1}s^{-1}$. Therefore, the organic substances in the wastewater may be oxidized and quickly dimerized by above reaction mechanisms. But a further increase of an amount of H_2O_2 would decrease the reaction rate due to scavenger effects.

Therefore, the decomposition rates were slower than those for the ozonation process in case of molar ratio greater than 1.0 because of scavengers for OH radicals. But the formation of OH radicals would be enhanced at low ratio of less than 0.5 at pH 7 when an ozone concentration was 45.6 mg/l·min and the concentration of hydrogen peroxide was 0.08 M. Fig. 8 shows that TMP and the permeate flux increased by approximately 4% and 7% in comparison with the case of input ozone concentration of 45.6 mg/l·min in the different phenol solution of 0.7 M, respectively. This indicates that more advanced oxidation with

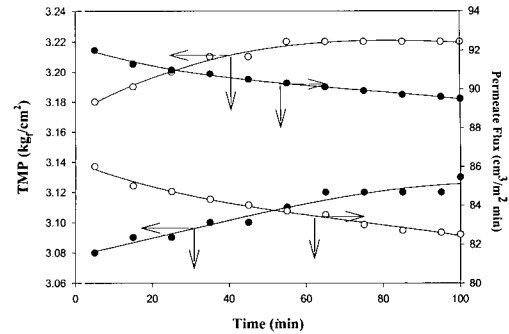


Fig. 8. Effects of TMP by the different molar ratio of H_2O_2/O_3 ●; 45.6 mg/l·min O_3 + 0.088 M H_2O_2 , ○; 45.6 mg/l·min O_3 .

hydrogen peroxide made less fouling in the membrane, but we think the effects for preventing the fouling were not significant.

4.2. Application into the wastewater treatment

1) Pretreatment of wastewater

Above equations of Eqs. (13)~(19) 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 [7]. 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 reactor mechanism shown in Eqs. (13)~(19). Therefore, the removal efficiency of organic substances can be dependent upon by input amount of hydrogen peroxide [8]. Because this is 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 and OH . 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

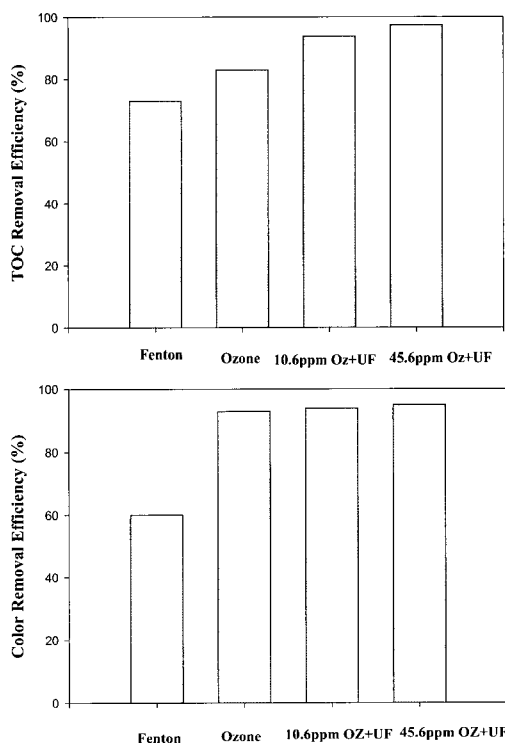


Fig. 9. TOC removal effects by ozone-mediated membrane process in the wastewater
Upper side: TOC removal efficiency,
Lower side: Color removal efficiency.

would make TOC increase oppositively. Therefore, it is important to remove organic substances by appropriate amount of hydrogen peroxide and ferrous sulfate at optimal pH.

Experiments were first carried out to test the effects of various amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 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 effect of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 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. Fig. 9 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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, respectively. This indicates that there exists the optimal condition of the ferrous sulfate and hydrogen peroxide, that is, the mole ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{H}_2\text{O}_2$ is approximately 0.1.

The removal efficiency of TOC was obtained by 71% using Fenton's oxidation under the condition above.

The amount of ozone supplied by the PCI ozone generator could be conveniently controlled by the air flow rate at a fixed current input of 1.2 A. The effect of ozone on the wastewater about the removal of TOC was compared between before and after Fenton's treatment. Apparently, its effect on the TOC and color removals by Fenton's oxidation was very drastic. For example, for the wastewater with an initial TOC concentration of 556.4 mg/l, TOC removal was very high at 80.9% in the absence of ozone. But the corresponding TOC removal by ozonation without Fenton's process was 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. This is due to the fact that the removal efficiency was dependent upon the amount of ozone available in the wastewater for the same ozone gas flow rate. To achieve an enhanced TOC removal, the ozonation after Fenton's method was more effective to remove TOC by 25%. To meet this discharge requirement, a membrane process was selected and tested in the present work as a final treatment step for effluent of wastewater from the ozone contactor. Although the TOC and color removal for the ozone contactor was much improved, it was still not sufficient to sustain a good treatment. To remedy this deficiency, the effluent of wastewater was treated in the ozone-mediated membrane process. Therefore, the more advanced technique to obtain the removal efficiency of more than 99% is definitely needed.

2) Effects of ozone in the hollow fiber membrane process (in case of wastewater)

The dyestuffs in the textile wastewater were easily altered during ozonation as manifested by rapid disappearance. The phenolic chemical compounds of dyestuff molecules could easily decompose under ozonation as shown in Table 1(a), they

generate more organic molecules in the wastewater. The increase of organic molecules generated by ozone regardless of the structures of dyestuffs or altered ones made the filtration in the porous membrane easy, this indicates the increase of flux in the membrane.

The dyestuffs in the wastewater used in the present study had structures with multiple rings and side chains of Benzidine polyazo-dye and Bromamine acid anthraquinon-dye as shown in Table 1 (b) and (c). When the structural rings are opened up or the side chains including a phenol compound, they were severed by ozonation as manifested by rapid color disappearance over 50%. Many previous investigations have shown that the ozonation was highly effective in breaking down the straight, unsaturated bonds in the dye molecules, causing rapid decolorization of wastewater. However, the ring opening or side chains generated a large amount of small chemical molecules in the solution by the ozonation. This accounts for the highly effective color removal of ozonation, but considerably less efficient TOC removal. Alteration of dyestuff molecules regardless of the original dyestuffs or altered ones were then oxidized [9]. And then, the organic substances were more degradable and generated small molecule organic compounds by the oxidation of an ozone. As a result, the color however can be effectively removed around 60% by Fenton's oxidation only, and such a ozone-supported color removal was increased from 60% to 84%. 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.

Fig. 10 shows the results of input ozone concentrations of 10.6 mg/l · min and 20.0 mg/l · min in comparison with those of 45.6 mg/l · min. TMP in case of input ozone of 10.6mg/l · min reached to 3.5 kgf/cm², the slope proportionally increased 8.55×10^4 , 1.13×10^3 , 9.17×10^3 as the ozone concentrations decreased from 45.6 mg/l · min, 20.0 mg/l · min to 10.6 mg/l · min, respectively. Therefore, TMP sharply rised in comparison with

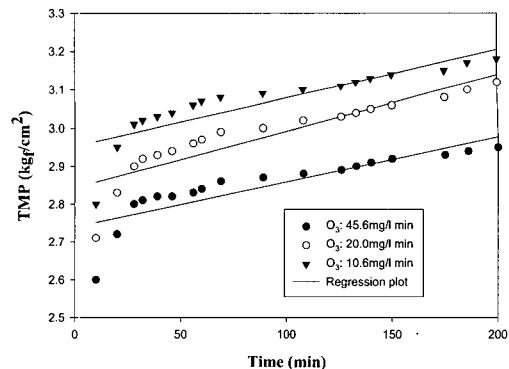


Fig. 10. Effects of TMP in the different ozone concentrations of between 10.6 mg/l · min and 45.6 mg/l · min in the wastewater treatment.

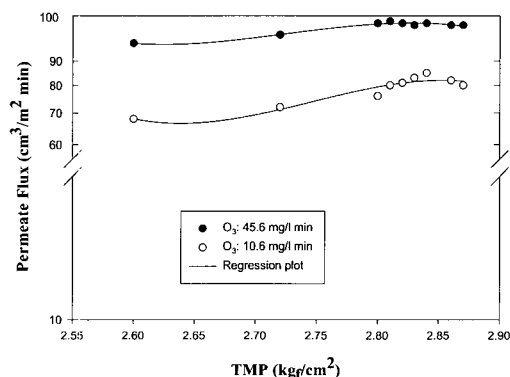


Fig. 11. Permeate flux vs. TMP in two different input ozone concentrations of 10.6 mg/l · min and 45.6 mg/l · min.

case of phenol solution, indicating that the transmembrane pressure in more pollutants' solution required more. As TMP increased, the permeate flux increased in higher concentration of input ozone and became constant and slightly decreased in lower ozone concentration after passing a time as shown in Fig. 11. This conclusively indicates that the ozonation would make the membrane prolong the period to reach the membrane-fouling rather than having a significant role to prevent the membrane fouling completely.

The corresponding TOC removal by ozone-mediated membrane as shown in the Fig.9 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 liter/min of ozone gas. The removal efficiencies of TOC in the membrane process was overall 93.8% in case of the wastewater treated by 10.6 mg/l · min of input ozone. But the removal efficiencies of TOC were increased by 95.1% and 97.5% in case of 20.0 mg/l · min and 45.6 mg/l · min of input ozone. The higher removal efficiency in the membrane process in comparison with Fenton's oxidation/ozonation would be speculated that better removal efficiency of TOC occurred due to the higher flux condition in the porous membrane by higher ozone concentration.

5. Conclusion

Experiments were conducted to investigate the treatment by ozonation in the membrane process. Emphases were placed on examining the performances characteristics of the combined treatment process. Results from all experimental runs revealed that:

1. The flux rate increased about 12% as the input amount of ozone increased from 10.6 mg/l · min to 45.6 mg/l · min in the synthetic phenol solution.
2. More ozonation was effective to subdue membrane fouling due to less requirement of TMP in the synthetic phenol solution.
3. TMP and the permeate flux increased by approximately 4% and 7% in input ozone concentration of 45.6 mg/l · min and 0.08 M hydrogen peroxide in comparison with the case of input ozone concentration of 45.6 mg/l · min in the synthetic phenol solution. The results were not significant to prevent the membrane fouling.
4. As TMP increased, it was found that the

permeate flux increased in higher concentration of input ozone and became constant and slightly decreased in lower ozone concentration after passing a time and the ozonation would not have a significant role to prevent the membrane fouling.

5. Addition of membrane process did little improvement of color removal over that by ozonation. In fact, the removal efficiency over 91% can be achieved.
6. Based on Fenton's oxidation/ozonation/membrane filtration mechanism, the TOC treatment efficiency of wastewater got a good result of 98%.

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