

## Single-phase membrane ozonation of hazardous organic compounds in aqueous streams

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### Abstract

The use of ozone to treat hazardous organic wastes in water is limited by the low solubility of ozone in water. The use of semipermeable nonporous silicone capillary membranes to transfer ozone nondispersively into an aqueous phase and ozonate organic species has been studied for the single pollutants phenol, nitrobenzene and acrylonitrile. Preliminary experimental results are presented here to demonstrate the efficacy of such a process using silicone capillary membranes. The substantially larger  $a$  (surface area per unit volume of device) ( $15.3 \text{ cm}^2/\text{cm}^3$  in the case of module 2) that this membrane ozonator provides leads to a significantly larger value of mass transfer parameter compared to those in conventional equipments. For iodometric consumption of ozone, the value of  $k_p a$  in presence of reaction was found to be  $5.8 \times 10^{-3} \text{ s}^{-1}$  in module 2 compared to calculated values of  $1.058 \times 10^{-3} \text{ s}^{-1}$  for a packed column containing Raschig rings 1.3 cm in size and  $3.22 \times 10^{-4} \text{ s}^{-1}$  for a bubble column operating under comparable superficial gas and liquid velocities.

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### 1. Introduction

Ozonation has been traditionally employed as a method for disinfecting drinking water. It was also realized that improvements in taste and odor accompanied the disinfection of water by ozone [1]. In recent times, ozone has been used to treat hazardous organic compounds in wastewater and ground water tainted with organic species [2]. Under the rubric of advanced oxidation processes (AOP), a number of studies on the oxidation of hazardous wastewaters have been carried out using a combination of  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  and UV and  $\text{H}_2\text{O}_2$  [2, 3].

The use of ozone in water purification is limited by its low solubility in water [2] and hence the mass transfer rate from the gas phase to the liquid phase. Also the

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relatively low concentration of ozone in the gas phase is a major factor in the design of the gas–liquid contactor. The design of the contactor is therefore focused on maximizing  $O_3$  transfer from the gas phase to the aqueous phase. Conventional contacting equipments include bubble contactors, turbine mixers, injectors, packed columns and spray chambers. Most of them suffer from low values of  $k, a$  and plugging problems due to precipitated salts. The treatment of higher strength wastewaters using ozone, however, has not received much attention primarily because of the recalcitrance of some of the compounds to oxidation and the amount of ozone that can be delivered per unit volume of reactor per unit time.

The work shown here began using a two-phase ozonation study [4] as a basis for implementing novel nondispersive microporous membrane-based techniques [5,6] for the treatment of organic pollutants in wastewater. Such a strategy led to the development of a novel membrane reactor for two-phase ozonation [7,8]. This reactor had two sets of hollow fiber membranes, commingled in a cylindrical shell filled with a low vapor pressure, high molecular weight fluorocarbon (FC phase) fluid. Ozone-containing oxygen was fed through one set of fibers having a nonporous wall and wastewater containing organic pollutants (e.g. phenol, nitrobenzene, etc.) was fed through the second fiber set which had microporous walls. The FC phase had a high solubility for ozone and served as a reaction medium allowing the destruction of organic species which had partitioned from the aqueous phase into the organic phase. The reaction products partitioned into the aqueous phase and the gas phase (e.g.  $CO_2$  is likely to exit primarily via the gas phase).

Such hollow fiber membrane-based two-phase reactors provide a very high surface area per unit reactor volume and lead to the development of very compact, nondispersive devices. A few questions can be raised at this stage. Is an intervening FC phase required for ozonation? What would happen if the wastewater were ozonated directly, without the FC phase, but with an intervening nonporous membrane to keep apart the gas and liquid phases? Since ozonation of wastewater is controlled primarily by the aqueous phase resistance, would not the high value of  $a$  of a membrane device enhance the  $k, a$  for the transfer of a sparingly soluble gas such as ozone into water, compared to traditional devices?

Preliminary results of single-phase ozonation of synthetic wastewaters in a nonporous capillary membrane module are reported here. Silicone membranes were chosen, since they have a large permeability for oxygen [9] (and therefore a comparably large permeability for ozone) and the silicone polymer (polydimethylsiloxane) is relatively resistant to oxidation. The hazardous organic pollutants studied were phenol, nitrobenzene and acrylonitrile.

## 2. Experimental details

The experimental procedure involved first the fabrication of the single-phase membrane ozonator. Nonporous silicone capillaries, (1.6 mm ID, 2.4 mm OD for module 1 and 0.30 mm ID, 0.64 mm OD for module 2, silastic medical-grade tubing, Dow Corning, Midland, MI) were laid out in the form of a mat. The ends of the

capillaries were tied together and inserted in a transparent FEP shell (0.61 cm ID, 1.03 cm OD; Cole Parmer, Chicago, IL) equipped with barbed polypropylene Y-fittings (Cole Parmer, Chicago, IL) at the two ends. The two fiber ends were then potted using Armstrong epoxies, C4-D for the internal tube sheet and A2-A for external hardening (Beacon Chemical Co., Mt. Vernon, NY). The epoxies were allowed to cure for seven days before ozonation experiments were implemented. Details of the reactors, used in the study, have been provided in Table 1.

Ozone was generated using a polymetrics (Colorado Springs, CO) ozone generator, using a pure oxygen gas cylinder (extra dry) (Matheson, E. Rutherford, NJ). The aqueous phase was analyzed for the pollutants using a high performance liquid chromatograph (HP 1090A, Hewlett Packard, Paramus, NJ) equipped with a Hyper-sil ODS glass column (10 cm long and 3 mm dia., Chrompack, Bridgewater, NJ). Table 2 shows the HPLC conditions used to detect and determine the concentration of pollutants in the aqueous phase.

The experimental loop was set up as shown in Fig. 1. Aqueous feed was prepared by spiking deionized water with a pure liquid sample of the pollutant to give the necessary feed composition in the case of nitrobenzene and acrylonitrile. The aqueous feed was passed through the shell side of the reactor at a constant flow rate from a feed reservoir pressurized with N<sub>2</sub> (extra dry) (Matheson, E. Rutherford, NJ). The operating gas flow rate of the ozone generator was high and therefore most of it was bypassed directly to the fume hood. A sample of it, however, was sent to the membrane ozonator. Ozone-containing oxygen was passed through the tube side of

Table 1  
Details of silicone capillary membrane based ozonators

Module no.	Dimensions of capillaries ID/OD (mm)	Active length (cm)	No. of capillaries	Shell volume (cm <sup>3</sup> )	a <sup>a</sup> (cm <sup>2</sup> /cm <sup>3</sup> )
1	1.58/2.41	28.0	4	39.77	2.39
2	0.305/0.610	21.59	97	20.6	15.28

<sup>a</sup> Specific surface area per volume of ozonator based on OD of capillary.

Table 2  
HPLC conditions for the organic compounds studied

Compound	Wavelength (nm)	Composition <sup>a</sup> (%)	Flow rate (cc/min)
Phenol	254	40AC/60H <sub>2</sub> O	0.4
Nitrobenzene	254	40AC/60H <sub>2</sub> O	0.4
Acrylonitrile	210	40AC/60H <sub>2</sub> O	0.4

<sup>a</sup> Acetonitrile (AC) and water were used as the mobile phase. A sample loop of 10 μl was used.

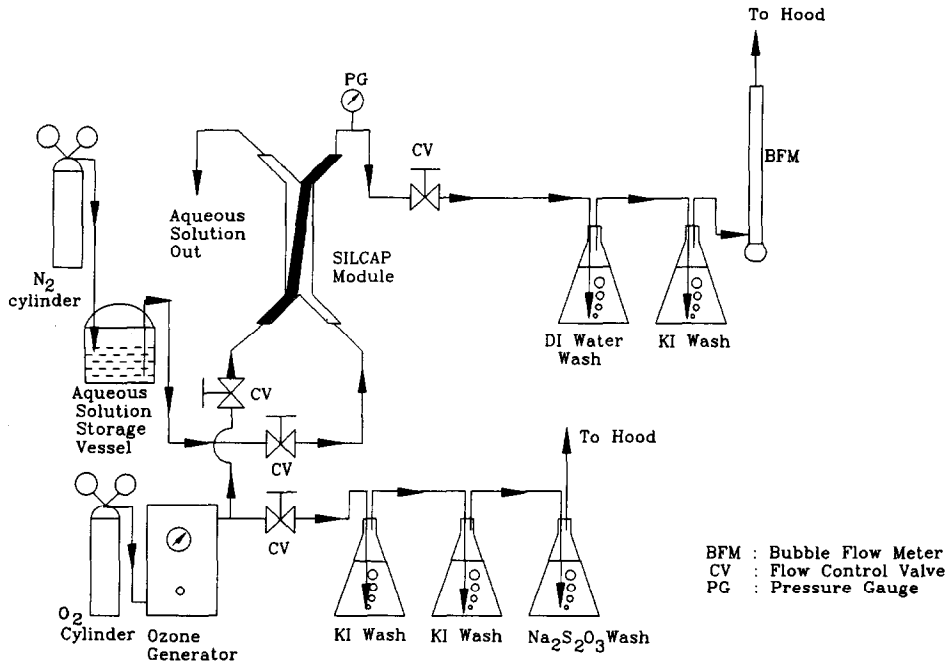


Fig. 1. Schematic of the experimental loop for single-phase membrane ozonator.

the module; the pressure and flow rate were controlled by means of the control valve at the inlet and the needle valve at the outlet, respectively. The gas stream was washed with KI (potassium iodide) solution before being exhausted to the fume hood. Conversion  $X_A$  of any pollutant  $A$  was calculated by the change in the concentration of the pollutant in the aqueous phase divided by the aqueous feed concentration of the pollutant:

$$\text{Conversion } X_A = \frac{C_A^{\text{IN}} - C_A^{\text{OUT}}}{C_A^{\text{IN}}}, \quad (1)$$

where  $C_A$  refers to aqueous phase concentration of pollutant  $A$ .

To determine the value of  $k_L a$  under conditions of conversion of KI to  $I_2$ , the experimental loop was modified as shown in Fig. 2. Instead of the aqueous feed, a 2 wt% KI solution was passed through the shell side at a measured flow rate. The KI solution was collected, acidified with  $H_2SO_4$  and titrated against  $Na_2S_2O_3$  (sodium thiosulfate) of known concentration with starch solution used as an indicator. The gas exiting the reactor was passed through a wash bottle containing a known quantity of KI solution for a measured duration of time. A 10 ml sample of the KI solution was then titrated against  $Na_2S_2O_3$  to give the concentration of ozone exiting in the gas phase (since the amount of iodine released is directly proportional to concentration of ozone in the gas phase).  $k_L a$  was determined from the experimental

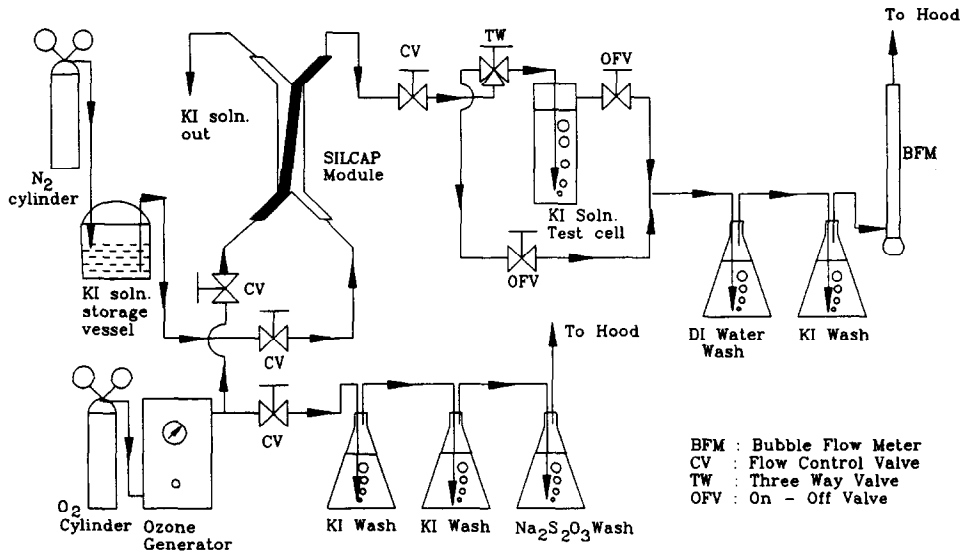


Fig. 2. Schematic of the experimental setup to measure mass transfer coefficient in single-phase membrane ozonator.

data in the following manner:

$$k_r a = H k_g a = H \frac{\text{permeation rate of } O_3}{\left( \frac{p_{O_3}^{\text{in}} - p_{O_3}^{\text{out}}}{\ln(p_{O_3}^{\text{in}} / p_{O_3}^{\text{out}})} \right)}, \quad (2)$$

Where  $H$  = Henry's law constant,  $p_{O_3}$  = partial pressure of ozone,  $k_r$ ,  $k_g$  = mass transfer coefficients based on liquid and gas phases respectively; and  $a$  = specific surface area per unit volume of reactor.

### 3. Results and discussion

The experimental results are presented and discussed here in the following order: membrane ozonator performance for single organic pollutants in the aqueous phase; determination of module  $k_r a$ , and comparison with conventional ozonation techniques. The hazardous organic compounds studied were phenol, nitrobenzene and acrylonitrile.

The performance of the membrane ozonator in dealing with aqueous streams containing a single pollutant will be illustrated now. The degradation of phenol was studied in module 1 while that of nitrobenzene and acrylonitrile was studied in module 2.

The reactor module 1 was operated with the aqueous phase containing phenol on the shell side. The exiting steady state aqueous phase concentrations reported here

were obtained after running the reactor continuously for 3–4 h (samples were analyzed however every 15–20 min to determine the steady state. The observed behavior eliminated any possibility of a steady state resulting simply from membrane extraction). During an earlier part of the study the reactor was operated with the aqueous phase on the tube side as shown in Fig. 3. At low aqueous flow rates this was found to lead to slugging problems which reduced the contacting efficiency and therefore further experiments with the aqueous phase on the tube side were discontinued. It is seen from Fig. 3 that the conversion of phenol in the membrane ozonator was high about 50% at aqueous phase flow rates of 1 ml/min, as the aqueous phase was passed through the tube side. For water flowing on the shell side at a lower flow rate, 0.1 ml/min, phenol conversions of 85% were observed.

Fig. 4 shows the performance of module 2 for nitrobenzene as the liquid and gas flow rates were varied. At the lowest aqueous phase flow rates conversions of 70% were observed. It should be noted here that since the  $a$  of module 2 was considerably higher than that of module 1, the efficiency of ozonation was higher, indicated by the lower gas flow rates needed to achieve comparable pollutant conversions (comparing Figs. 3 and 4 and assuming all other factors, viz. stoichiometric ratios and reaction chemistries are similar). The average residence times of the aqueous phase in module 2, as compared to module 1, were smaller by a factor of almost 2 (for an aqueous flow rate of 0.1 ml/min, the residence time in module 1 would be about 400 min as compared to 200 min in module 2); yet due to the higher  $a$  of module 2, the performance was comparable based on the pollutant conversion.

Fig. 5 shows the degradation of acrylonitrile in module 2 for varying aqueous phase and gas flow rates. Conversions in the range of 60% were observed for aqueous feeds of 0.1 ml/min and gas flow rates of 30 ml/min. The reasonably high aqueous feed

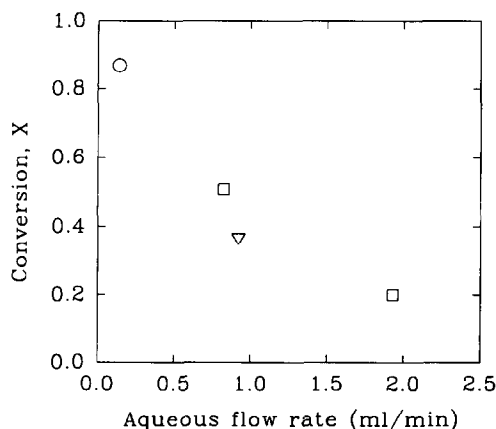


Fig. 3. Degradation of phenol in the single-phase membrane ozonator. Module used: Module 1. Aqueous flow on shell side. (○) Average gas flow rate = 39.4 ml/min. Aqueous feed composition = 107 ppm. Aqueous flow on tube side. (▽) Average gas flow rate = 47.0 ml/min. Aqueous feed composition = 102 ppm. (□) Average gas flow rate = 56.8 ml/min. Aqueous feed composition = 89 ppm.

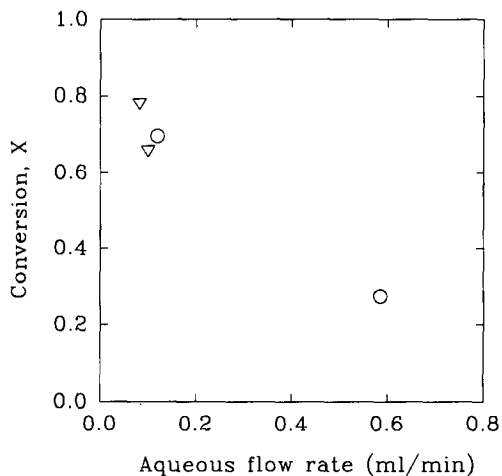


Fig. 4. Degradation of nitrobenzene in the single-phase membrane ozonator. Module used: Module 2. Aqueous flow on shell side. Aqueous feed composition = 111 ppm. ( $\nabla$ ) Average gas flow rate = 19.3 ml/min. ( $\circ$ ) Average gas flow rate = 25.6 ml/min.

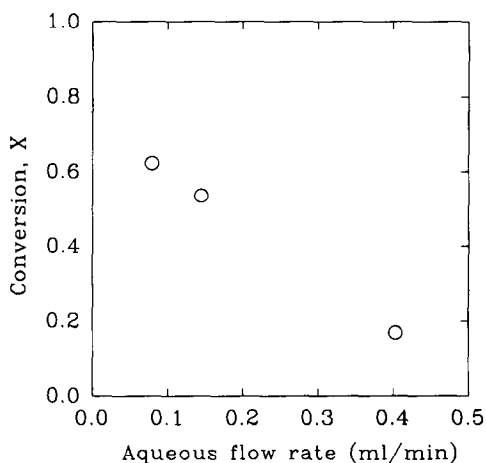


Fig. 5. Degradation of acrylonitrile in the single-phase membrane ozonator. Module used: Module 2. Aqueous flow on shell side. Aqueous feed composition = 206 ppm. Average gas flow rate = 30 ml/min.

concentrations must also be noted, since it implies the use of such ozonators in handling low to medium strength wastewaters. During the experiments, especially when the reactor was operated at low aqueous phase flow rates, the silicone capillaries were exposed to the harsh oxidizing environment of ozone and the other ongoing oxidation reactions for prolonged periods of time (at least 100 h). Since the data reported here were taken, the reactor has been employed to degrade other

Table 3  
Results of mass transfer experiments for module 2

No.	KI containing aq. flow rate (ml/min)	Gas flow rate (ml/min)	O <sub>3</sub> exit concentration <sup>a</sup>		Permeation rate <sup>b</sup> (mg/cm <sup>2</sup> s)	$k_g^c$ (mg/s cm <sup>2</sup> atm)	$k_r a^d$ (s <sup>-1</sup> )
			(mg/l)	(atm)			
1	11.4	13.7	35.40	$19.69 \times 10^{-3}$	$3.85 \times 10^{-6}$	$1.55 \times 10^{-4}$	$5.82 \times 10^{-3}$
2	9.6	17.5	36.33	$19.26 \times 10^{-3}$	$3.84 \times 10^{-6}$	$1.56 \times 10^{-4}$	$5.843 \times 10^{-3}$

To obtain  $k_r$ ,  $k_g$  was multiplied by a Henry's law constant of  $1.18 \times 10^5$  atm cm<sup>3</sup>/g mol (at 25 °C [1]). The permeation rate was determined from the gas flow rate, measured in the absence of the test cell and corrected for the gas flow rate when the test cell was in place.

<sup>a</sup> Exit concentration was corrected to 0 °C and 14.7 psia from 29 °C and 16.7 psia.

<sup>b</sup> Average permeation area considered = 417.78 cm<sup>2</sup>.

<sup>c</sup> The feed gas concentration was 58.42 mg/l ( $30.97 \times 10^{-3}$  atm).

<sup>d</sup>  $a = 15.3$  cm<sup>2</sup>/cm<sup>3</sup>.

compounds. This reflects the ruggedness and durability of the membrane device with regards to its operation and chemical inertness.

The volume percent of ozone in the feed gas phase under the experimental conditions was determined to be 2.9% [10]. The relevant data and other information pertaining to the calculation of  $k_r a$  has been shown in Table 3. The  $k_r a$  for the module (module 2) in the presence of the ozone–KI reaction was found to be  $5.8 \times 10^{-3}$  s<sup>-1</sup> ( $a = 15.28$  cm<sup>-1</sup>) at a superficial liquid velocity of 0.2 cm/s and a superficial gas velocity of 4 cm/s. At a comparable superficial liquid velocity, in a packed column containing Raschig ring packings of nominal size 1.3 cm and  $a$  of  $3.64$  cm<sup>-1</sup>, Onda's correlation [1] predicted a  $k_r a$  of  $4.6 \times 10^{-4}$  s<sup>-1</sup> without any chemical reaction. Langlais et al. [1] have suggested that for iodometric reaction conditions, this  $k_r a$  should be multiplied by the enhancement factor 2.3 for fast irreversible first-order reactions to yield  $1.058 \times 10^{-3}$  s<sup>-1</sup>. For similar superficial gas velocities, bubble columns at 20 °C [1] yielded a  $k_r a$  of  $1.4 \times 10^{-4}$  s<sup>-1</sup> under nonreaction conditions and therefore a value of  $3.22 \times 10^{-4}$  s<sup>-1</sup> under similar iodometric reaction conditions. Thus the  $k_r a$  value for the silicone capillary-based membrane ozonator under conditions of ozonation is a few times larger than those obtained in conventional ozonation equipment for similar superficial liquid and gas velocities.

#### 4. Conclusions

In view of stricter environmental regulations, there is an increasing need for efficient and economical devices to detoxify wastewaters containing hazardous organic compounds. The single-phase capillary membrane ozonator of this study appears to be highly suited for this purpose. Further it performs at much higher ozonation efficiencies compared to conventional ozonation devices. The preliminary study demonstrates the ability of the device to handle medium strength wastewaters (feed inlet concentration was on the average about 100 ppm for nitrobenzene and phenol and



about 200 ppm for acrylonitrile). This was achieved at the expense of high residence times of the order of  $\sim 200$  min at the lowest aqueous flow rates in module 2. The ozonation efficiency can be improved (and simultaneously the residence times reduced) by using finer capillaries resulting in an increased surface area per unit volume for the reactor. Using transverse flow, the value of  $k_t$  can be increased drastically. Also the present device (module 2) can be used in treating drinking water and ground water tainted with organic species. Since these devices allow gas–liquid contacting in a nondispersive manner, they do not require compressors or excessive energy in order to contact the gas and liquid phases efficiently. Further if there is any precipitation of salts (especially in the treatment of groundwater), the associated problems of deposition and clogging will be absent since these membranes are nonporous in nature.

The potential use of such an ozonator suggests further study into the fate of the organic pollutants and the long-term durability of the silicone substrate. The ramifications of using secondary oxidizing agents, viz.  $H_2O_2$ , need to be explored since the synergy may serve to extend the operational window of such a device to treat higher strength wastewaters at reasonably low residence times.

Since this is a modular membrane device, scale-up problems are not envisioned. There is an added advantage of independent control of the gas and liquid phases suggesting that the ozone dosage rates can be adjusted to obtain the best possible degradation performance. The role (if any) of bypassing or channelling of liquid flow on the shell-side on the reactor performance is unknown at this time. Any stripping of volatile organic pollutants into the gas phase is unlikely to be a problem since there will be reabsorption downstream and subsequent destruction.

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