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Experiment and modeling of advanced ozone membrane reactor for treatment of organic endocrine disrupting pollutants in water

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ABSTRACT

An advanced ozone membrane reactor that uses membranes for ozone distribution, reaction contact and selective water separation was used for ozone treatment of a recalcitrant endocrine disrupting compound in water. Experiments and model calculation were employed to examine the ozonation of phthalate in the new reactor. Experimental results showed that fast ozone mass transfer rate is responsible for membrane reactor's superb performance compared with a semibatch reactor. Selective water removal further enhanced phthalate conversion and TOC removal by concentrating the pollutants in the reaction zone. Clean water was produced by membrane separation. Mathematical model was used to investigate the effect of membranes, reactor design and reaction operation on pollutant conversion and removal.

1. Introduction

There is growing evidence that a large number of chemical compounds found in common household products ranging from medicines, cosmetics and personal care products, and household cleansers, can survive state-of-the-art wastewater treatment processes to contaminate surface and ground waters [1–10]. Many of these compounds are endocrine disruptors and studies carried out in 2001 [11] and 2003 [12] showed that a large numbers of endocrine disrupting chemicals (EDCs) survive conventional drinking water treatment processes to persist in finished, potable water. Several of the compounds were even found in samples of human blood, milk and urine [13]. Although health risk from chronic exposure to EDCs in humans has not been adequately addressed, their effects on normal hormonal processes is well documented and there is extensive evidence of their adverse effects in wildlife [14]. It is particularly disturbing that most studies in animal models [15] showed that early life stages are the most vulnerable to the actions of EDCs, putting pregnant women and children at greater risk [16].

Ozone and membrane processes are technologies that showed the best promise for treatment of EDCs in water [17,18]. However, ozone treatment alone suffered from slow mineralization rates [19] and the UV/O_3 and O_3/H_2O_2 used by various authors [20–22] to remedy this shortcoming are often expensive and complex. Nanofiltration and reverse osmosis membrane can remove most EDCs [23,24], but the separated EDCs require further treatment. In addition, membrane fouling is a concern [25]. Ozone has been used in membrane to alleviate membrane fouling by organic matters [26,27] and improves membrane filtration processes [28]. Shanbhag et al. [29] explored in their early work the use of a silicone capillary membrane for ozone distributor for treatment of chemical micropollutants in water. More recently Karnik et al. [30] employed a catalytic membrane based on ultrafiltration and ozonation for drinking water treatment. This work examines an advanced ozone membrane reactor for treatment of recalcitrant organic EDCs in water. The membrane reactor uses membranes for ozone distribution, reaction contactor and water separation in a compact unit that synergistically combines ozone oxidation and membrane separation to achieve greater treatment efficiency. The use of multi-functional membrane reactor was shown to benefit gas-phase and liquid phase reactions [31–38]. Indeed, prior works showed the new membrane reactor increased mineralization rate, improved ozone utilization, reduced membrane fouling and enhanced clean water production [39,40]. This study investigates the design of the reactor and membranes using a mathematical model to guide the optimization and scale-up the process

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Nomenclature

A_c	cross-sectional area (m^2)
A_g	surface area for gas distribution (m^2)
A_m	membrane surface area (m^2)
C	concentration ($mol\ m^{-3}$)
C_o	feed concentration ($mol\ m^{-3}$)
Cv	convective flux ($mol\ m^{-2}\ s^{-1}$)
D	diffusivity ($m^2\ s^{-1}$)
De	depletion factor
Di	diffusive flux ($mol\ m^{-2}\ s^{-1}$)
En	enhancement factor
N_i	organic compounds permeation flux ($mol\ m^{-2}\ s^{-1}$)
No	total number of species
N_w	water permeation flux ($m^3\ m^{-2}\ s^{-1}$)
P'	water permeance ($m^2\ bar^{-1}\ s^{-1}$)
P''	EDC permeance ($m^{-1}\ s^{-1}$)
Pe	Peclet number
$\dot{Q}$	gas feed rate ($m^3\ s^{-1}$)
R	reaction rate ($mol\ m^{-3}\ s^{-1}$)
R_m	membrane intrinsic resistance ($bar\ s\ m^{-1}$)
R_{cp}	concentration polarization ($bar\ s\ m^{-1}$)
X	dimensionless radial location in the membrane support
K	ozonation reaction rate constant ($m^3/mol\ s$)
a_b	specific interfacial area of gas bubble ($m^2\ m^{-3}$)
k_{Dd}	ozone direct decomposition rate constant (s^{-1})
k_{Di}	Ozone indirect decomposition rate constant ($mmol^{-0.5}\ s^{-1}$)
k_H	Henry's constant of ozone
k_L	mass transfer coefficient of ozone from gas to water ($m\ s^{-1}$)
p	Vapor pressure (bar)
$\dot{q}$	gas feed flux through s.s. membrane ozone distriutor ($m\ s^{-1}$)
r	radius (m)
r_{in}	inner radius of membrane support (m)
r_{out}	outer radius of membrane support(m)
r'	transformed radius (m)
t	time (s)
v	superficial flow velocity ($m\ s^{-1}$)
$\bar{v}$	superficial flow velocity per unit reactor height (s^{-1})
x	mole fraction
y	dimensionless concentration
z	stoichiometric coefficient

Greek symbol

α	fouling factor ($m^2\ s\ bar\ mol^{-1}$)
β	gas volume holdup
δ_{Al}	alumina support thickness (m)
δ_m	membrane thickness (m)
ε_{Al}	porosity
τ	dimensionless time

Subscripts

i	different species
ref	reference
w	water
A	ozone
B	endocrine disrupting compound
BP	degradation byproducts

Superscripts

g	gas
j	the jth alumina support sub-model
p	permeate
r	retentate
Al	alumina support phase
G	bulk gas phase
L	bulk liquid phase
Sat	saturated vapor pressure (bar)

for practical application in the treatment of EDCs-contaminated water.

2. Experiment and model

2.1. Potassium hydrogen phthalate (KHP) ozonation reaction kinetics

The KHP ozonation reaction scheme in Fig. 1 was mainly based on the experimental results [39], with some of the pathways deduced from literature reports on dimethyl phthalate (DMP) [41]. The main intermediates and products include large intermediates with molecular structure similar to KHP (I1), intermediate ketones, aldehydes and carboxylic acids (I2) and simple carboxylic acids such as formic and acetic acids (I3) that have low UV detection. The reaction rate equations are fitted to a second order reaction kinetic typical for ozonation reactions [42,43]. The reaction rates were obtained from a semibatch reactor using a glass sparger for ozone distribution. Ozone was produced from pure oxygen by corona discharge in Wedeco ozone generator. The gas pressure and ozone concentration were measured by an on-line pressure gauge and ozone analyzer (BMT 964®), respectively. The ozone gas volumetric flowrate was regulated by a Teflon flow meter (Cole Parmer®). The 250 mL semibatch reactor was filled with 150 mL of 250 ppmC KHP solution and sparged with 200 sccm 120 ppm O_3/O_2. Samples were taken at fixed time intervals and purged with nitrogen gas. 10 mL samples were poured into a 50 mL conical flask and the dissolved ozone was measured by iodometric titration. 0.3 g KI and six drops of 0.4 M sulfuric acid were added to the solution and titrated using 0.002 M $Na_2S_2O_3$ solution and starch indicator. The pH was measured and the organics were analyzed by Water Acquity UPLC equipped with BEH C_{18} column and a PDA eλ UV–vis detector and Shimadzu total organic analyzer (TOC-V CSH). The concentrations of the intermediates and products were obtained by calculating their sensitivity factors (SF_i) from Eqs. (1) and (2).

$$TOC_{Cal} = \sum_{i=1}^{N} SF_i x PA_i \quad (1)$$

$$SSE_{TOC} = \sum_{i=1}^{N_{rt}} (TOC_{Mea} - TOC_{Cal})^2 \quad (2)$$

where PA_i is the peak area of species i (AU); SF_i is the sensitivity factor for species i (ppmC/AU) obtained at minimum SSE_{TOC} (i.e., squared errors of TOC); TOC_{Cal} is the calculated TOC (ppmC); TOC_{Mea} is the measured TOC (ppmC); and N is number of species.

2.2. Advanced ozone membrane reactor experiments

A schematic drawing of the advanced ozone membrane reactor is shown in Fig. 2. Ozone gas bubbles were fed by a 35 mm long porous stainless steel membrane (i.e., 0.2 μm) welded to the stainless steel reactor shell. The stainless steel membrane was purchased from Mott Metallurgical and had inner and outer diameters of 12.5