

ENDOCRINE DISRUPTION CHEMICALS (EDCs) DEGRADATION IN AN ADVANCED OZONE MEMBRANE REACTOR – EXPERIMENTAL & MODELING STUDY

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Abstract

A study of ozonolysis degradation kinetics of EDCs in two phase gas-liquid system has been performed in a semi-batch reactor observing Total Organic Carbon (TOC) degradation. TOC degradation alone may not be a sufficient parameter because multiple/complex kinetic concept is needed. This has been accomplished with experimental work. Reaction perturbed evolution and decay of the initial substance and its degradation by-products have been observed based on Glasser-Hildebrandt concept. TOC degradation and multiple/complex reaction kinetic parameters have been determined from percentage TOC consumption and HPLC area response rationalization based on carbon balance. These kinetic information have been incorporated to model and simulate ozone membrane reactor system using (i) mass balance approach and (ii) widely used continuity equation. The derived model answers the values of the characteristic parameters such as efficiency, molecular weight cut-off and enhancement for EDCs remediation in ozone membrane reactor.

Keywords

complex kinetic; Membrane reactor modeling; Dynamic simulation; Ozonolysis; Enhancement factor.

Introduction

Ozonolysis is a technology of interest to handle the problem of EDC materials. The ineffectiveness of today's conventional biological waste water treatment plants results occurrence of EDCs in surface water bodies. The potential risk of chronic exposure to these EDCs contaminated water in human has not been adequately addressed to date, but their effects on normal hormonal process are well documented and there is strong evidence of their adverse effects in wild life^{1,2}. To solve this problem, degradation study (i.e., reaction kinetics) of EDCs has been carried out by the authors^{3,4}. They used ozone as an oxidant and observed reactant's concentration gradient. However, they compromised extent of TOC mineralization, which is very important for legislative compliance. In course of ozonolysis, even though reactant degrades but at the same time Degradation By Products (DBPs) are formed and

decayed. This may be even more harmful than the reactant (i.e., EDC) itself². A number of studies have been reported in the published literature⁵⁻⁷ on reaction (ozonolysis) rate constants of many potent EDCs. Most of these studies have been performed in small scale at low temperature⁸⁻⁹. They disregarded effect of heat and mass transfer. These are very important for pilot plant and industrial scale implementation. EDCs ozonolysis depends on reaction kinetics. This plays a key roll in describing effect of experimental conditions on conversion, reaction mechanism and transition states from reactant to carbonaceous mineralization. These information are needed to derive mathematical models that can simulate and predict characteristics of chemical reaction in a wide range of process conditions. This work endeavors incorporation of reaction kinetics taking into account heat and mass transfer effect to construct a mathematical model. The model describes and predicts performance of a compact ozone membrane reactor to treat EDCs of interest. Optimization tools are used to

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enhance mineralization of these refractory EDCs. So that the EDCs borne lethal effect to human and wildlife would be reduced. This is important to meet compliance which may be imposed given the need for strong legislation to protect health and environment. Semi-batch operation is superior to both plug flow and continuous operation²⁸. It is suitable to determine reaction kinetics due to its flexibility over a wide range of process conditions. Moreover, flow through reactor model can be developed using parameters (kinetics) independently determined from batch and semi-batch experiments (Kim et al., 2007). This study is based on modeling and simulation of a plug flow membrane reactor using intrinsic kinetic parameters determined from semi-batch experiment for performance prediction and optimization.

Problem Descriptions

Issues need to be addressed in modeling and simulation are model equations, kinetic co-efficient and numerical solution. Model equations need to be compatible with the system on one hand while on the other hand the right kinetic co-efficient is required to validate sets of modeling equations. For ease of compatibility, suitable modeling equation can be ascertained choosing a misfit criterion followed by selecting consistent design objective function to effect model sensitivity (i.e., extensive variables). Once the model is established, it can be validated using kinetic co-efficient independently determined from laboratory scale experimentation. Afterwards extensive variables as described in design objective function can be varied for simulation and prediction purposes with appropriate Boundary conditions (B.Cs).

Materials and Methods

Materials

All common chemicals used in semi-batch ozonolysis study were of the highest grade available commercially. Double de-Ionized (DDI) water was used to prepare 100 ppm standard aqueous solution using aliquot of required solute and was stored in refrigerator at 4oC to prevent microbial degradation. All other low concentration solutions were prepared by diluting this standard solution. Detailed material and experimental methods of semi-batch ozonolysis have been covered in a separate article by Islam et al., 2010¹¹.

Analytical Methods

HPLC analysis is carried out for simultaneous detection and quantification of semi-batch ozonolysis products. A HPLC PDA, Waters series liquid chromatograph (USA) instrument was used for analysis. Detection was accomplished with a waters 2475 fluorescence wavelength of 285 nm for all reactants and DBPs used in this study. A water 5 μm XTerra[®] column RP18 analytical column was used for reverse phase separation with 200 μm sample loop. The mobile phase solvent profile was 55% formic acid buffered with 0.05% H_3PO_4 and 45% acetonitrile (diluted 3:1 in water) for 10 minutes at a constant flow rate of 1 ml/min for each

sample specimen. The method was isocratic and the column was reestablished to the run time by passing the same mobile phase solvent for 5 minutes. DFS (DCP) and DBPs were evolved at different retention time as depicted in Figure 1.

Numerical Methods

Modeling has been done according to the standard methods described by Ridlehoover and Seagrave¹⁰. According to this method, semi-batch kinetics has been incorporated to model and simulate a plug flow ozone membrane reactor. Model equations have been derived applying fundamental mass balance approach¹² and continuity equation¹³. Model validation has been accomplished by determining kinetic co-efficient from semi-batch experiment. Once the model is validated within acceptable error as described in the published literature¹⁴, simulation has been done over a wide range of process conditions for prediction purposes.

Theoretical background

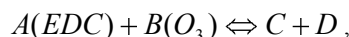
Semi-batch ozonolysis

Theoretical basis is based on Semi-Batch Reaction mechanism for gas (O_3) – liquid (EDCs) two phase system [Figure 3(a)] and can be described by two film mass transfer theory²⁷. Ozone from bulk gas phase is transferred to: (i) gas-gas film interface, (ii) gas film-gas/liquid interfacial area of mass transfer and (iii) gas/liquid interfacial area of mass transfer to bulk liquid. Mass transfer constrains are resistance associated in each phase in series and can be characterized by concentration and diffusivity of initial substances.

Predictive modeling as derived to determine semi-batch kinetics is based on the following assumptions: (i) the system is semi-batch transient state where gas (ozone) is continuously filled-in stagnant liquid column with homogenous EDC solution, (ii) most of the resistance to mass transfer resides on liquid film only at gas (ozone) - liquid interface, (iii) gas (ozone) is dosed in excess and its concentration does not change in course of reaction.

Reaction Mechanism

Commensurate with two film theory, gas (O_3) and liquid (dilute EDC solution) react instantaneously in liquid film [Figure 3(a)] formed at gas (O_3) – liquid interfacial area of rising bubbles diffused through Sparger assembly. Dissolved gas (O_3) and EDC do not co-exist in liquid phase. The gas phase reactant transferred to gas-liquid interfacial area of mass transfer react instantaneously at a plane in liquid film where concentration of both of the reactants are zero^{16,17}. In this case reaction kinetics exists in liquid film formed at gas-liquid interfacial plane¹⁸. According to reaction mechanism [Figure 3(a)] and for the reaction scheme:



mass balance for the component A (EDC) at the gas-liquid interface can be written as¹²,

$$0 + r_{A,TOC} \cdot V(t) = 0 + \frac{dN_{A,TOC}}{dt} \dots\dots\dots(1)$$

where symbols are defined in the notation section. The sets of underlying kinetic equations, derived intrinsic kinetic coefficients and corresponding mass transfer coefficients are shown in the **Table 1**¹¹.

Multiple/complex kinetic reaction mechanism

Multiple/complex kinetic reaction mechanism is essential to describe evolution and decay of initial substances and DBPs precisely in ozonolysis. Generic DFS-Ozonation kinetic model can be derived using HPLC results⁵ and van de Vusse kinetics modified by Glasser et al., 1987²⁹. Applying Glasser-Hildebrandt concept, multiple/complex reaction kinetic co-efficients have been determined from percentage TOC consumption and HPLC area response rationalization based on carbon balance as shown in **Table 2**. Good agreement between model prediction and experimental results has been obtained as shown in Figure 3(b).

Ozonolysis in dual membrane reactor

Modeling has been done for a plug flow dual membrane reactor¹³ using kinetic co-efficient independently determined from sub-section 4.1. Incorporation of membrane (i.e., ZSM-5/Silicalite -1) in dual membrane reactor involves reaction in annular region followed by membrane separation. Reaction mechanism is the same as described in sub-section 4.1. The modeling is based on the following assumptions¹⁵: (i) uniform temperature plug flow operation, (ii) diffusive transport through the membrane, (iii) permeation through membrane is proportional to concentration gradient and flow in annular and tube side of the membrane, (iv) Membrane is inert to the reaction and ozonolysis reaction take place only on the annular region in the AMOR, (v) gas (i.e., ozone) is dosed in excess and consistent size bubbles are distributed into fluid domain over the entire annular reactor volume, (vi) at any cross-section in the reaction domain along the length of the reactor process variables (i.e., concentration of initial substances, temperature, viscosity etc.) do not change, (vii) Gas (ozone) dosing does not affect overall bulk density of the fluid inside the reaction domain as a result effect of volume change is disregarded (viii) untransferred/trapped gas (O₃) does not affect overall reaction kinetics and (ix) physical systems where all mass balance equations have been derived are two-phase gas-liquid macroscopic and gas bubbling does not affect overall bulk density of fluid where widely used continuity equation is applicable.

Mathematical modeling has been done by applying: (i) fundamental mass balance approach across differential volume ΔV in reaction domain and (ii) and continuity equation around REV in the reactor.

Application of approach (i) for overall mole balance of component A across a differential volume ΔV in the annular region along the length of the membrane reactor would lead¹²,

$$F_{A,in.at.vol^m V} - F_{A,out.at.vol^m (V+\Delta V)} + r_A \cdot \Delta V = 0 \dots\dots\dots(2)$$

Application of approach (ii) for plug flow membrane reactor would lead¹³,

$$\frac{\partial \rho}{\partial t} + \nabla \bullet (\rho v) + \nabla \bullet (D \nabla \rho) = 0 \dots\dots\dots(3)$$

Assuming steady flux across the interfacial mass transfer film and narrow reaction channel, effect of diffusion/dispersion term can be neglected and simplified PDE can be written as¹⁹,

$$\frac{\partial \rho}{\partial t} + \nabla \bullet (\rho v) = 0 \dots\dots\dots(4)$$

Governing equation in both approach (i) and (ii) can be further simplified for dynamic fluid property change relationship and for concentration gradient due to ozonolysis can be expressed as,

$$\frac{\partial C_A}{\partial t} = r_{\tau A} \dots\dots\dots(5)$$

Multiple/complex kinetics mechanism has been employed in membrane reactor modeling for DFS ozonolysis as shown in Table 2. Additional diffusion term has been inserted in the corresponding balance equations to reflect permeation.

For plug flow reactor system we can write,

$$C_T = \sum_{i=1}^n C_i \text{ and } F_i = F_T \times \frac{C_i}{C_T}$$

Overall dynamic mass balance around membrane reactor module has been deduced from continuity equation as described below²⁰:

$$\frac{\delta F_T}{\delta t} + \nabla \cdot (F_T \cdot U) = -\nabla \cdot (J_T) + S_k$$

.....(6)

Assuming negligible change in species flux due to convection in radial direction and no flux production then, equation (6) reduced to

$$\frac{\delta F_T}{\delta t} = -\nabla \cdot (J_T)$$

.....(7)

Equation (7) can be re-written in the form

$$mF \cdot \frac{\delta C_T}{\delta t} + S_m \cdot D_m \cdot mF = 0$$

.....(8)

Where S_m is membrane effective separation area, D_m is diffusivity of the compound in the membrane and mF is the feed flux.

This is basically complete mass balance around reactor module whose simplification can reproduce mass flux conservation around the reactor module as,

$$F_F = F_P + F_T$$

.....(9)

Flux balance approach can deduce membrane characteristic dynamic diffusivity as,

$$D_m = \frac{mP}{mF \times S_m}$$

.....(10)

Membrane overall TOC removal efficiency can be calculated from the following equation^{14,21,22},

$$\frac{TOC}{TOC_0} = \frac{(1-R) \left(\sum_{i=1}^n C_i \right) \times F_P + R \times \left(\sum_{i=1}^n C_i \right) \times F_T}{\left(\sum_{i=1}^n C_{i,0} \right) \times F_F}$$

.....(11)

$$MWCO = \frac{R \times \sum_{i=1}^n (C_i \times MW_i)}{\sum_{i=1}^n C_i}$$

.....(12)

Membrane pervaporation reactor

In membrane pervaporation, dominant mechanism is physical separation. This takes place due to concentration gradient resulting from applied vacuum and membrane action for a given flux. The modeling is based on the following assumptions: (i) Plug flow operation, (ii) Thin film boundary layer is established at solid-liquid interfacial area of mass transfer on membrane site, (iii) Negligible concentration gradient between membrane site liquid phase boundary layer of mass transfer and bulk liquid once Pervaporation operation is established and (iv) Vapor phase concentration of solute A is negligible with compared to bulk liquid (this is the case for organic Pervaporation). Mass balance is the same as described in equation (2) and for the component A(EDC) in case of membrane Pervaporation,

$$\frac{dF_A}{dV} + P_{pev,A} = 0$$

.....(13)

Which simplification for dynamic concentration gradient would lead,

$$\frac{dC_a}{dt} = -\left\{ \frac{1}{K_{Over..all}} \right\} \times \left\{ \frac{P_m}{tk} \right\} \times Ca$$

.....(14)

$K_{over all}$ can be calculated from²³:

$$F_{A,over..all} = K_{Over..all} \times \rho_f \times (C_f - C_p)$$

.....(15)

$$F_A^{boundary..layer} = K_l \times \rho_f \times (C_f - C_{Al})$$

.....(16)

$$F_A^{across\ membrane} = P_m \times \rho_f \times \left(\frac{C_{m,l} - C_{m,v}}{tk} \right) \dots\dots\dots(17)$$

From equation (15) to (17) we can get,

$$\frac{1}{K_{Over..all}} = \frac{1}{K_l} + \frac{tk}{P_m} \dots\dots\dots(18)$$

After determining membrane permeability, permeate TOC and TOC degradation efficiency for membrane pervaporation can be predicted from equation (14) and (11) respectively.

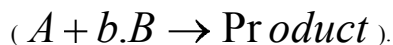
Modeling of membrane ozonation and membrane pervaporation system offer performance simulation. This is done over a wide range of process condition to optimize process variables. However, prior model validation is required with right kinetic coefficients from experimental work.

Model Solution and simulation

Detailed algorithm for ozone membrane reactor model development together with corresponding numerical solution as well as simulation package are presented in Figure 2(a) & 2(b). POLYMATH 6.10 build 261 software was used to simulate the model setting corresponding B.Cs after validation with experimental results. Moreover, significance of membrane action can be uncoupled from membrane enhancement co-efficient for ease of farm process optimization. Simplified degree of freedom is also considered during model development. According to phase rule, degree of freedom = components – number of phases + 2. In our system TOC is considered as variable and due to excess gas dosing effect of gas phase is disregarded. As a result, degree of freedom for this simplified system is 2. Therefore TOC concentration and ozonation duration are the least number of variables that need to be solved in modeling and simulation work.

Membrane enhancement co-efficient

Membrane enhancement co-efficient has been determined for Gas (O₃) – Liquid (EDCs solution) reactive system



Pseudo first order reaction in liquid phase is assumed. Two distinct scenarios are tested namely: (1) For ozonolysis alone without membrane separation¹⁶:

$$Ha = \delta_l \left(\frac{K_A}{D_{Al}} \right)^{0.5} = \frac{(D_{Al} \cdot K_A)^{0.5}}{K_{Al}}; n = 1$$

where, A is liquid phase reactant, D_{Al} is ozone/reactant diffusivity in water (m²/s), K_A is pseudo first order reaction rate constant (1/s) and

$$K_{Al} = V_l \times \left(\frac{K_{O3}}{a.n} \right); E = \frac{Ha}{\tanh(Ha)}; \text{ for a}$$

function Ψ such that, $E = \frac{\Psi}{\tanh(\Psi)}$, calculate

Ψ and the value is iterative Hatta number consistent with the particular reaction; $\Psi = Ha \times \left(\frac{E_i - E}{E_i - 1} \right)^{0.5}$,

calculate actual reaction enhancement “E_i” and (2) for ozonolysis coupled with membrane separation: above procedures have to be followed and in addition, calculate more consistent Hatta number if refinement is necessary,

i.e., $E = \frac{Ha}{\tanh(Ha)}$. After determining Enhancement

(E_i) and Hatta number (Ha) from scenario 1 and 2, where 1 is without membrane effect and 2 is with membrane effect, “reaction rate” or “membrane co-efficient” enhancement due to ozonolys coupled with membrane separation can be calculated by the following equation²⁴:

$$r_{over..all}(or, \Phi_{over..all}) = (k_L \cdot a) \times C_{TOC..remaining}(or, C_{TOC} / C_{TOC0}) \times \left\{ \sqrt{\left(\frac{Ha^2}{4(E_i - 1)} + \frac{Ha \cdot E_i}{E_i - 1} + 1 \right)} - \frac{Ha}{2(E_i - 1)} \right\} \dots\dots\dots(19)$$

Results and discussion

Modeling and simulation for ozone membrane reactor is carried out for (i) model validation, (ii) simulation and (iii) optimization.

Model validation

The model is validated with published data on KHP ozonolysis coupled with membrane separation and membrane pervaporation¹⁴ in case of ZSM-5/Silicalite-1 inorganic membrane. Figure 4(a) and 4(b) represent membrane dynamic TOC degradation efficiency. Good agreement between model prediction and experimental results have been achieved for residence time, tr>2.4 minutes. In most incidences, experimental data deviated from model prediction within $\pm 5\%$ error for membrane ozonolysis and membrane pervaporation which is acceptable.

Model simulation

Primarily the model as derived in section 4 and solved in section 5 is validated for KHP. Afterwards, the same model is used to predict degradation efficiency of another pharmaceutical EDC material, Diclofenac Sodium in plug flow ozone membrane reactor. Results are shown in Figure 3(c).

This figure shows degradation efficiency of both initial substance, Diclofenac Sodium (DFS) and TOC as a function of residence time at different membrane rejection ratios namely: 100% (P0), 90% (R90) and 50% (R50) which correspond to Da 289, 260 and 146 respectively. From this figure it is clear that degradation efficiency of both initial substance (DFS) and TOC decrease with decreasing membrane rejection ratio. Steady DFS/TOC degradation efficiency was obtained after initial rapid declination before membrane started to exhibit steady rejection. This is due to increased high flux level was unable to sustain even for short period, and would normally have fallen back steady state level²⁵ after membrane start to exhibit steady state rejection. As a result characteristic initial drop-off of both initial substances and TOC degradation efficiency was modeled by extrapolation of model simulation data in the residence time interval $0 < t_r < 1.03$ minutes by developing corresponding empirical correlation consistent with model simulation²⁶.

Average molecular weight (Da) retained by the membrane increases with the increase in membrane rejection ratio as shown in Figure 4(c). From definition of Membrane Molecular weight Cut Off (MWCO) and from model simulation (Figure 4(c)) we can conclude that MWCO for KHP ozonolysis is around 190 Da and corresponding residence time around 5 minutes. This is obtained from the slope at the inflection points for 90% membrane rejection in KHP ozonolysis. From this characteristics curve it is possible to fix membrane rejection, molecular weight cut off and residence time (~5 min) for a given kinetics (table 2) in case of EDCs (i.e., KHP) ozonolysis.

Figure 4(d) is characteristic curve for dynamic membrane performance co-efficient enhancement. From this curve it is clear that increasing residence time beyond 1.5 minutes, membrane enhancement co-coefficients rapidly drop-off and membrane effects do not exhibit higher TOC degradation efficiency compared to that of ozonolysis alone without membrane separation. From this Figure, residence time used by Heng et al., 2006¹⁴ for most of membrane ozonolysis ($t_r \sim 2$ min) is justified. At lower residence time, ($t_r = 1$ to 1.5 min) membrane TOC degradation efficiency (co-efficient) is higher than that of ozonolysis alone without membrane separation.

Conclusion

Incorporation of semi-batch kinetics in plug flow ozone membrane reactor model has been carried out in research work. This model is successfully validated for industrial EDC, KHP within acceptable error ($\pm 5\%$). Mathematical

model indicated that it is possible to degrade other emerging pollutants (i.e., EDCs) effectively into harmless products using advance ozone membrane reactor where DFS was used as a model pollutant. This model can also be used as a process optimization tools for ozone membrane reactor performance prediction (figure 4(c)). This can answer critical issues (i.e., membrane rejection ratio, molecular weight cut-off) need to be addressed for suitable membrane development to affect desired function (i.e., O₃-EDC degradation). Membrane enhancement co-efficient can further confirm process parameter up to which membrane action will exhibit pollutants mineralization for the treatment of Endocrine disruption Compounds (EDCs) from water and was waste water.

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List of Symbols

Nomenclature

a	Interfacial area (m ²)
A	Initial substance (mg C.L ⁻¹)
A.U.	Arbitrary unit
B	DPB1 (mg C.L ⁻¹)
C	DPB2 (mg C.L ⁻¹)
C	Concentration (mg C.L ⁻¹)
D	DPB3 (mg C.L ⁻¹)
Dm	Membrane diffusivity (m ²)
D	Diffusivity (m ² .min ⁻¹)
Da	Dalton (g/mol)
E	Activation energy (Joule/mole/K)
E	Enhancement (-)
F/mF/J	Flux (mg.m ⁻² .min ⁻¹)
Ha	Hatta number (-)
k	Specific rate constant (min ⁻¹)
K	Co-efficient (min ⁻¹)
K	Overall reaction rate constant (min ⁻¹)
K _{overall}	Overall pervaporation co-efficient (mg.min.m ² .L ⁻²)
k _{La}	Mass transfer coefficient overall (min ⁻¹)
k _{AL}	Diffusivity at gas liquid interface (m.s ⁻¹)
n	No. of bubbles
N	Molar concentration (mol.L ⁻¹)
P	Gas pressure (KPa(g))
Pm	Membrane permeability (mg.min.m ² .mx10 ⁻⁶ .L ⁻²)
r	Reaction rate (mg.L ⁻¹ .min ⁻¹)
R	Component flux due to diffusion (mg.m ⁻² .min ⁻¹)
R	Membrane rejection ratio (-)
S	Surface (m ²)
S	Net rate of flux production per unit volume (mg.m ⁻³ .min)

t	Time (min)
T	Temperature (K)
V	Volume (L)
v_0	Rate of change of volume (L.min ⁻¹)
exp/ext/Expt	Experimental
EDC	Endocrine Disruption Chemicals
KHP	Potassium Hydrogen Phthalate
MWCO	Molecular Weight Cut Off

(Greek) symbols

tk	Thickness of the membrane (m)
□	Difference (-)
δ	Partial differential (-)
δl	Film thickness (-)
∇	Gradient (m ⁻¹)
τ	Time scale (hr/min/s)
ρ	Density (Kg.m ⁻³)
Φ	Enhancement co-efficient (min ⁻¹)
ρ _f	Fraction

Subscripts

i, k, n	Substances
B.C.	Boundary condition
O ₃	Ozone
GL	Gas (ozone)-liquid (EDCs solution) interface
g	Gas
l	Liquid
TOC	Total Organic Carbon
F	Feed
P	Permeate
R	Retentate
0	Initial
f	Final

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Table1. Semi-batch EDC ozonolysis kinetics.

Rate equations	Derived intrinsic kinetics	Kinetic efficient, (M ⁻¹ .s ⁻¹)	co-K _A	Ozone – EDC (A) mass transfer	
				Rate equations	Co-efficient at 30°C
$\frac{dC_{A,TOC}}{dt} = r_A - \frac{v_0}{V} \cdot C_{A,TOC}$ $\frac{dC_{B,TOC}}{dt} = -K_{A,TOC} \cdot C_{A,TOC} \cdot C_{B,TOC} + \frac{v_0 \cdot (C_{B0} - C_{B,TOC})}{V}$ $\frac{dC_{C,TOC}}{dt} = K_{A,TOC} \cdot C_{B,TOC} - \frac{v_0}{V} \cdot C_{C,TOC}$ $\frac{dC_{D,TOC}}{dt} = K_{A,TOC} \cdot C_{A,TOC} \cdot C_{B,TOC} - \frac{v_0}{V} \cdot C_{D,TOC}$ $V = V_0 + v_0 \cdot t$ $X = \frac{C_{A,TOC} \cdot V_0 - C_{A,TOC} \cdot V}{C_{A,TOC} \cdot V_0}$ $K_{A,TOC}(T) = K_{A0} \times e^{\frac{E}{RT}}$	$\frac{C_{A,TOC}}{C_{A0,TOC}} = K_A \cdot r(t)$	<p>1.8927 × 10⁵ (30° C)</p> <p>1.3333 × 10⁵ (40° C)</p> <p>0.76 × 10⁵ (60° C)</p> <p>Value reported in the literature (Sein et al., 2008):</p> <p>10⁴ – 10⁶</p>		$C_m I I_n Cl_p N_q O_r Na_s + \eta \cdot O_3 \xrightarrow{H_2O} m \cdot CO_2 + \frac{(n+s-p-q)}{2} H_2O + sNaCl + qHNO_3 + (p-s)HCl + \eta O_2$ $[C_{EDC, remaining}] \times \left(\frac{3\eta O}{mC + nH + pCl + qN + rO + sNa} \right) = [C_{O_3}]$ $r_{overall} = K_{overall} \cdot [C_{EDC}]$ $r_{overall} = K_{O_3} \cdot K_{EDC} \cdot [C_{O_3}] \cdot [C_{EDC}]$ $r_{O_3} = -\frac{dC_{O_3}}{dt} = K_{O_3} \cdot [C_{O_3}]$ $\frac{dC_{EDC}}{dt} = -K_{EDC} \cdot [C_{EDC}]$ $m = \frac{dC_{O_3}}{dC_{EDC}}$ $K_{O_3} = a_{GL} \times K_L$ $a_{GL} = A_i \times n_i$ $K_L = \frac{K_{O_3}}{A_i \times n_i}$	<p>For B.Cs.:</p> <p>C_{A0,TOC}=100</p> <p>C_{A,TOC}= 59.6</p> <p>t₀ = 0</p> <p>t_f = 90</p> <p>and for,</p> <p>A_i = 3.14 × 10⁻⁶ m²</p> <p>n_i = 500</p> <p>K_{O3} = $\frac{0.00575}{\text{min}}$</p> <p>K_L = $\frac{3.662}{\text{m}^2 \cdot \text{min}}$</p>

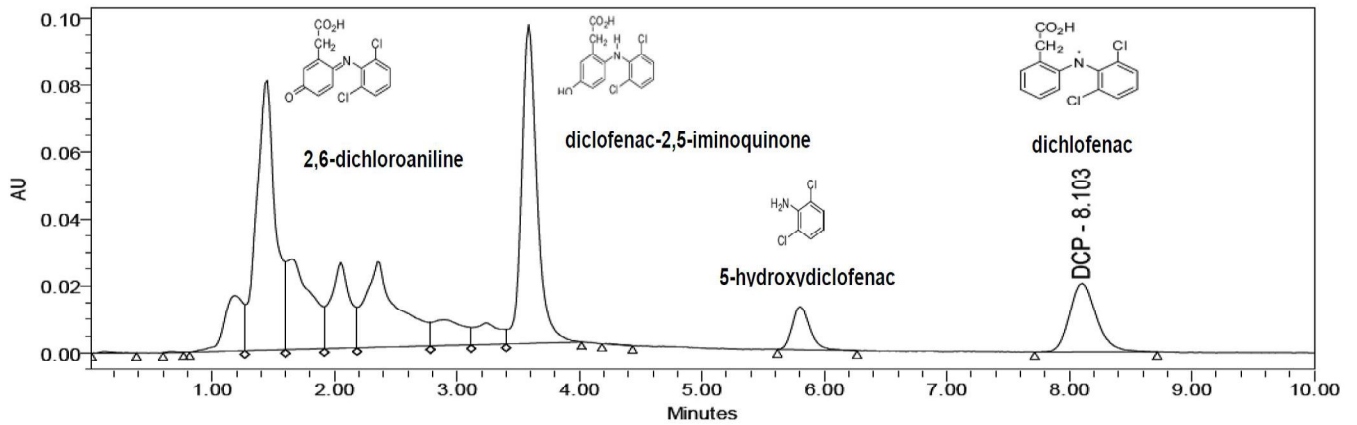
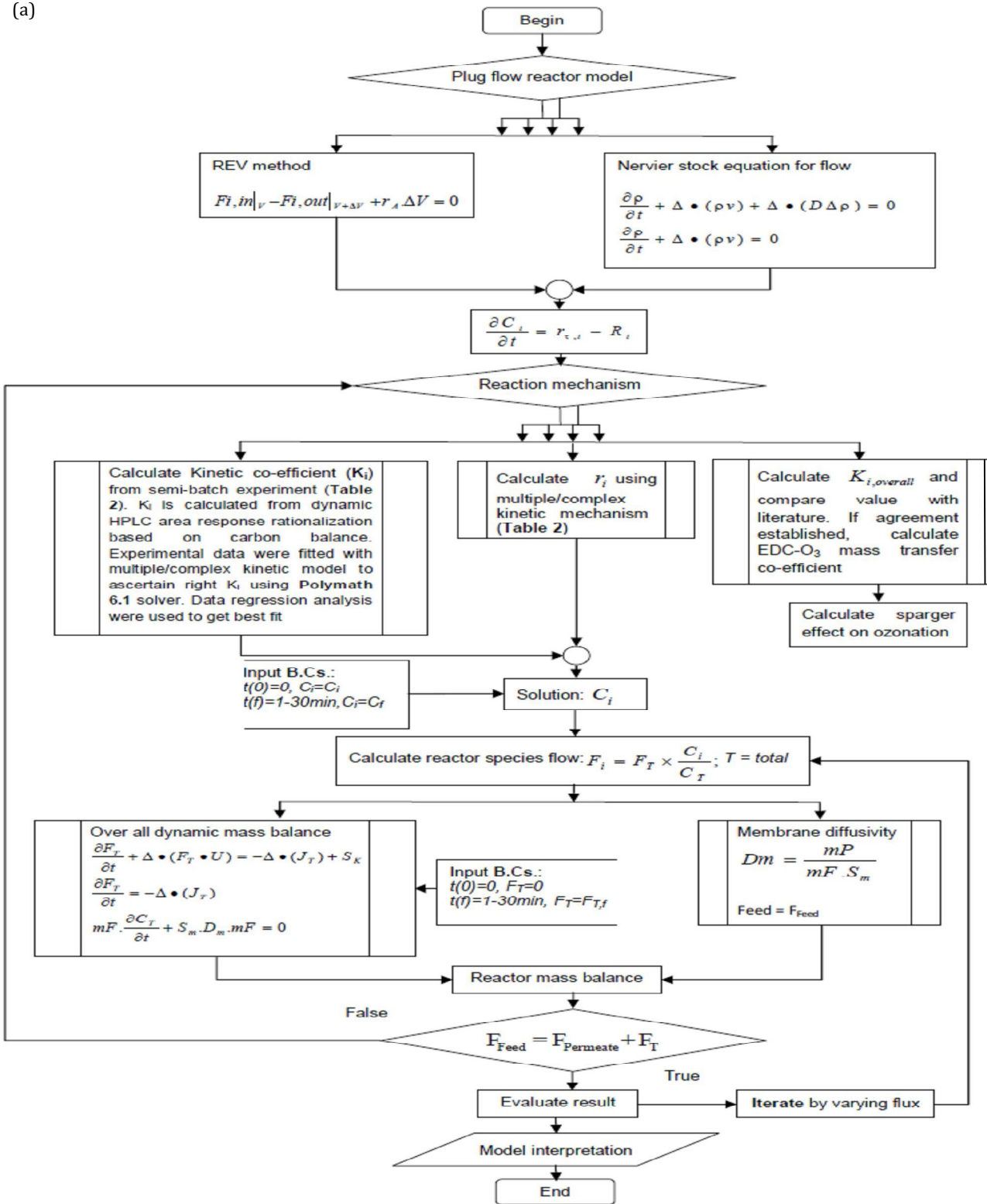


Fig 1. HPLC identification of reactant and DBPs during DFS ozonolysis.

Table 2. Multiple/complex kinetics

Multiple/complex reaction mechanism	Rate equation (r _i)	Kinetic co-efficient (1/min)	Comparison (Guha et al., 1995), (1/min)
$A(EDC_1) + O_3 \xrightleftharpoons[k_{-1}]{k_1} B \xrightarrow{k_2} C$ $\frac{1}{2} A + O_3 \xrightarrow{k_3} D$	$\frac{dC_A}{dt} = -k_1 C_A + k_1 k_B \cdot C_B - 2k_3 C_A^{1/2}$ $\frac{dC_B}{dt} = k_1 C_A - k_1 k_B C_B - k_2 C_B$ $\frac{dC_C}{dt} = k_2 C_B$ $\frac{dC_D}{dt} = 2k_3 C_A^{1/2}$	<p>For DFS:</p> <p>K₁ = 0.41</p> <p>k_B(k₋₁/k₁) = 0.0423</p> <p>k₂ = 0.043</p> <p>k₃ = 0.075</p> <p>For KHP:</p> <p>K₁ = 0.038</p> <p>k_B(k₋₁/k₁) = 0.0236</p> <p>k₂ = 0.018</p> <p>k₃ = 0.02</p>	<p>K_{Phenol} = 0.0576</p> <p>K_{Acrylonitrile} = 0.42</p> <p>k_{TCF} = 0.0246</p> <p>k_{TLN} = 0.092</p>

(a)



(b)

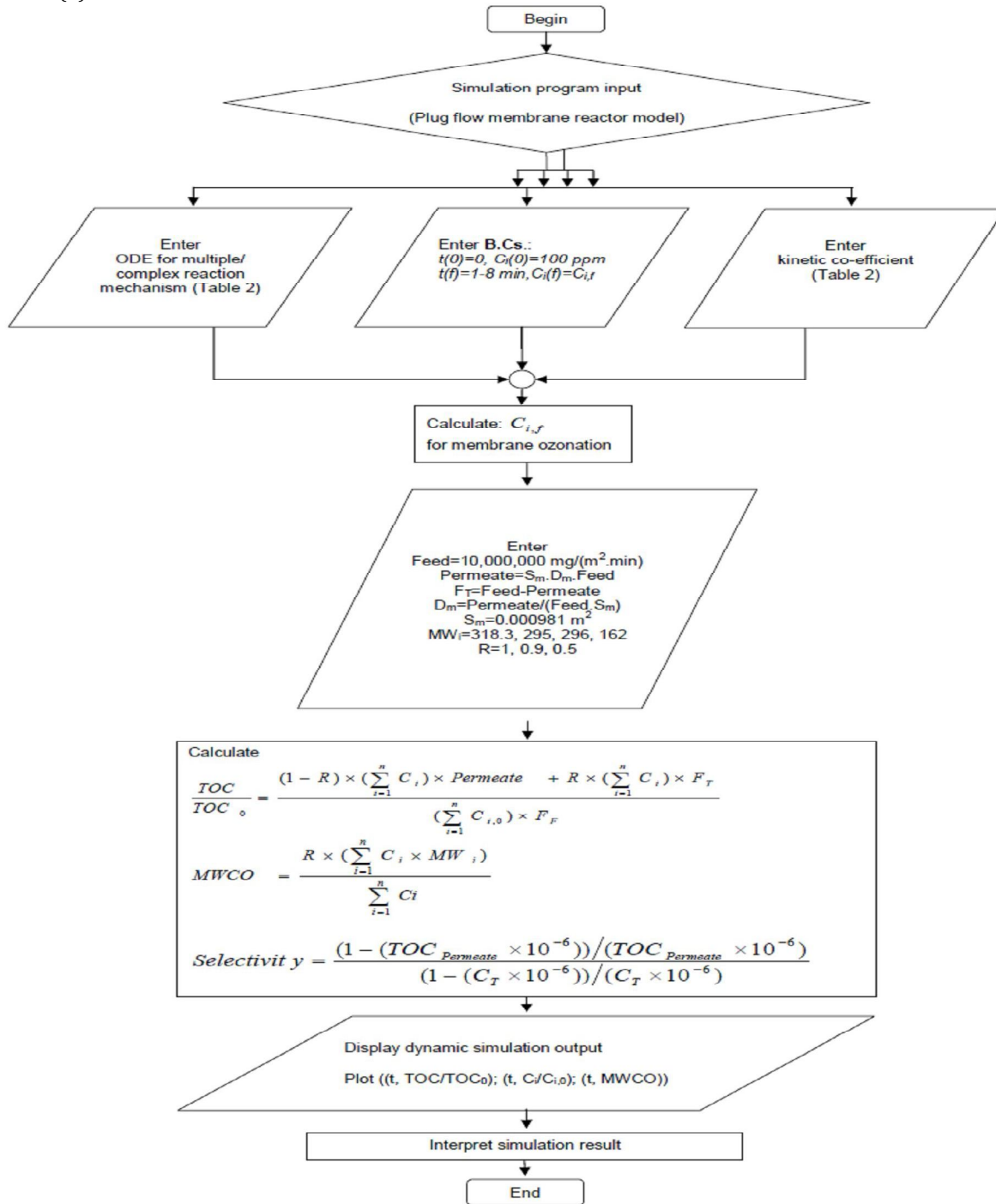


Fig 2. Ozone membrane reactor model development (a) algorithm and (b) simulation work.

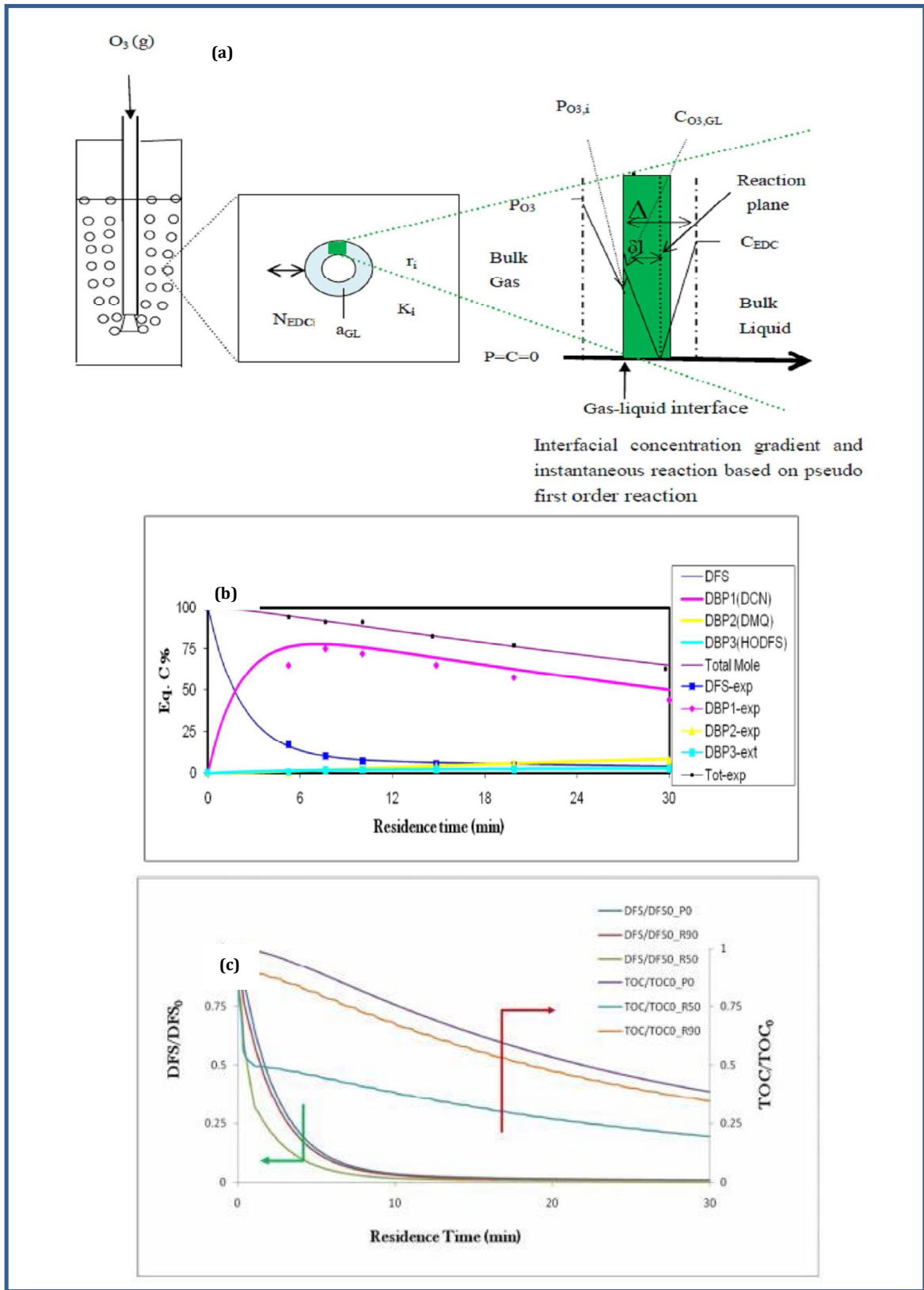


Fig 3. DFS ozonolysis in case of (a) Ozonolysis reaction mechanism at gas –liquid interface based on fast reaction, (b) Dynamic DBPs evolution in semi-batch ozonolysis and (c) Overall conversion and TOC degradation as a function of residence time obtained from model simulation in ozone membrane reactor. $[DFS]_0 = 100 \text{ mgC.L}^{-1}$, $T = 303 \text{ K}$.

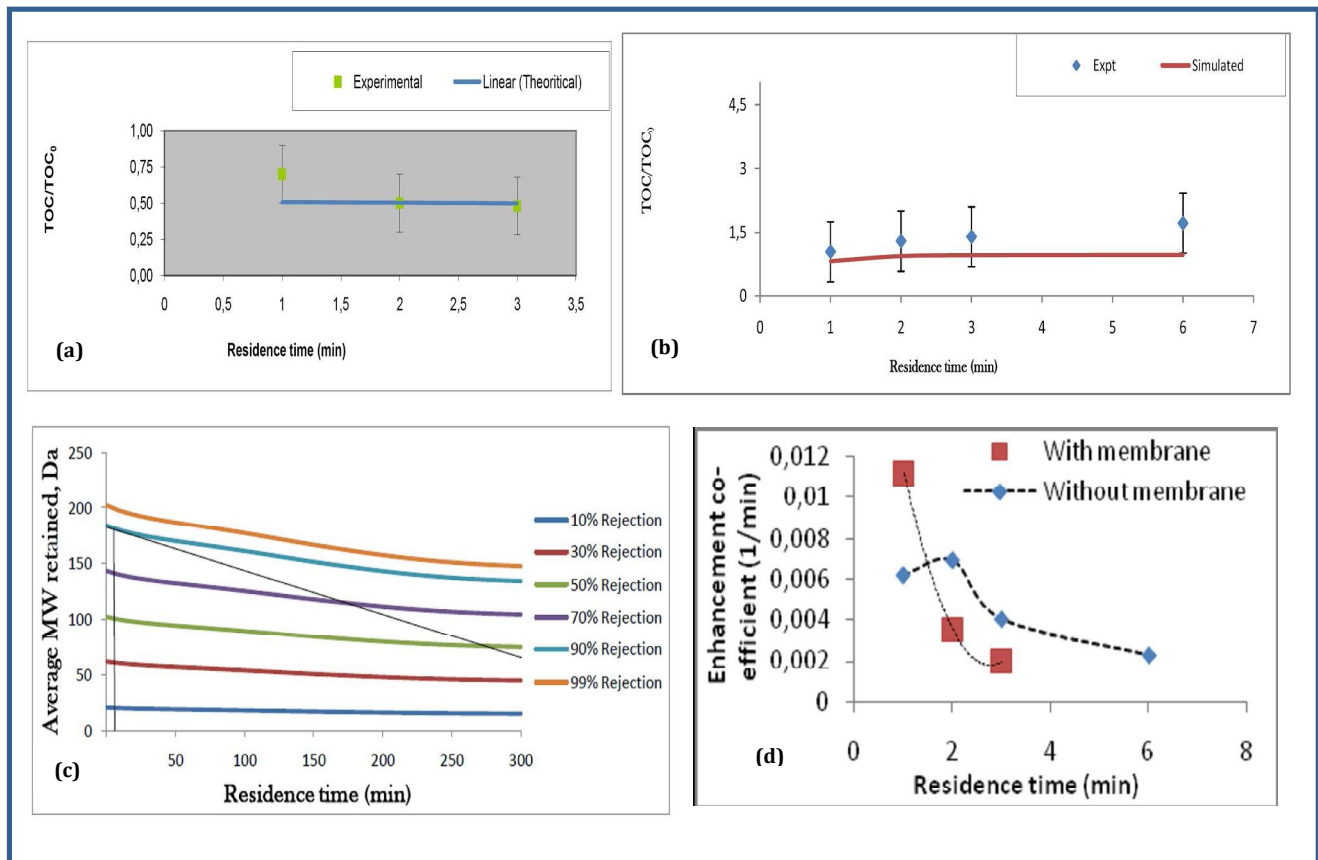


Fig 4. KHP ozonolysis in terms of (a) Membrane TOC removal efficiency Vs residence time for ozonolysis coupled with membrane separation. Solid line is obtained from model simulation and dots from experimental results, (b) Dynamic TOC degradation efficiency profile for Pervaporation in capillary membrane reactor for membrane permeability, $P_m = 0.004534$ and $K_{over\ all} = 0.00041$, (c) Dynamic average molecular weight retained by the membrane (Da) with different rejection for KHP ozonolysis as obtained from model simulation, (d) Dynamic reaction enhancement co-efficient with and without membrane separation for ozonolysis obtained from experimental results using equation 19. Dotted line is to guide the eyes.