



Photocatalytic reactors for treating water pollution with solar illumination: A simplified analysis for n -steps flow reactors with recirculation

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Abstract

The concentration of dissolved oxygen in water, in equilibrium with atmospheric air (ca. 8 ppm at 20 °C), defines the limits of all practical oxidizing processes for removing pollutants in photocatalytic reactors. To solve this limitation, an alternative approach to that of a continuously aerated reactor is the use of a recirculating system with aeration performed after every cycle at the reactor entering stream. As defined by the nature of a single recirculating step (the need of a reactor operation at a rather low concentration range), this procedure results in a very low photonic efficiency (thus requiring a large photon collecting area and consequently increasing the capital cost). The design engineer will have to resort to a series of several reactors with recirculation. This solution may then lead to a very high Photonic Efficiency for the entire process (i.e., a reduced light harvesting area) at the price of an increase in the required capital cost (due to the larger number of reactors). This paper provides a very simple analysis and analytical expressions that can be used to estimate, for a desired degree of degradation, a trade-off solution between a high number of reactors and a very large surface area to collect the solar photons.

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1. Introduction

Photocatalytic reactions employed to degrade most organic pollutants in aqueous solution require the presence of molecular oxygen (Ollis, 1991; Matthews, 1993; Sclafani et al., 1993). Lack of sufficient supply of oxygen

will eventually stop the reaction completely. It is accepted that in the reductive path of these reactions the presence of oxygen is necessary to trap electrons and thus to reduce the significance of the recombination of electrons and holes that are produced by illumination of the semiconductor catalyst. In a photocatalytic reactor it is in principle always possible to inject air to the water and to saturate the fluid with oxygen at equilibrium conditions. At ambient temperature (e.g., 20 °C) approximately 8 ppm of molecular oxygen (corresponding to

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Nomenclature

A	area (m^2)
A_{inc}	light harvesting area (m^2)
C	pollutant concentration (mole m^{-3})
$Da_{1,P}$	Photochemical Damköhler number
k	first order pseudo-kinetic constant (s^{-1})
N	number of moles (mole)
PI	photon Input ($\text{einstein m}^{-3} \text{s}^{-1}$)
q	photon flux ($\text{einstein m}^{-2} \text{s}^{-1}$)
Q	volumetric flowrate ($\text{m}^3 \text{s}^{-1}$)
R	recirculation ratio
t	time (s)
V	volume (m^3)
z	coordinate along the reactor (m)
X	reactor conversion

Subscripts

act	actual value
final	final value
max	maximum value
0	inlet value for a single or a series of reactors
R	relative to reactor
Rec	relative to recycle reactor
Sys	relative to system
Total	total value

Superscripts

in	inlet value
out	outlet value
PFR	relative to Plug Flow Reactor
Rec	relative to recycle reactor
Stat	steady state value
Sys	relative to system

Greek letters

ζ_{total}	total OPE ($\text{mole einstein}^{-1}$)
ζ_{act}	actual Observed Photonic Efficiency (Actual OPE) ($\text{mole einstein}^{-1}$)
ζ_0	initial OPE at reference conditions ($\text{mole einstein}^{-1}$)
ζ_x	local OPE ($\text{mole einstein}^{-1}$)
Ω	reaction rate ($\text{mole m}^{-3} \text{s}^{-1}$)
η	process efficiency
τ	mean residence time (s)

Special symbols

$\langle \rangle_{A_{\text{inc}}}$	denotes average value taken over the photon harvesting area
$\langle \rangle_{V_R}$	denotes average value taken over the reactor volume
0	initial/reference value

equilibrium with ambient air) will be dissolved. This means that without additional supply, only 8 ppm of the existing chemical oxygen demand (COD) can be treated. Polluted waters or wastewaters may certainly have a COD much higher than 8 ppm. If, for example, water with a COD = 400 ppm is considered and 90% COD removal is required, a series of 45 reactor steps with oxygen injections in between or a continuously aerated reactor will be needed to fulfill the desired objective.

Two different alternatives can be envisaged: (i) as indicated above, a continuous injection of air all along the reactor as achieved in the aerated cascade photoreactor (ACP) proposed by Sagawe et al., 2001 and (ii) a series of high recirculating flowrate reactors with air injection at the reactor inlet, limiting the COD conversion per pass to 8 ppm. For example, the recirculation flow rate can be adjusted in such a way that the incoming flow with a COD feed concentration of 400 ppm is mixed with the recirculating stream to produce a concentration of 48 ppm; assuming a COD conversion of 16.66% in the reactor, the outgoing stream will then have 40 ppm which is equivalent to 90% conversion of the feed. However, in the tubular reactor itself, the change in COD concentration is just 8 ppm. For more details on technical and economical aspects of solar detoxification reactors the reader can resort to very com-

plete descriptions existing in the scientific literature (Goswami, 1995; Goswami et al., 1997).

An analysis of the operation of the latter type of solution has been carried out in this paper, employing the Photonic Efficiency concept developed in previous contributions (Sagawe et al., 2003a; Sagawe et al., 2003b; Sagawe et al., 2004). It is the main approach of the concept to employ rather simple models to describe solar reactors (which are characterized by time dependent and unpredictable, i.e., variable illumination conditions) and real wastewaters (characterized by variable pollutant composition) and whenever possible, to search for analytical solutions. More elaborate models, the use of which is very often restricted to model pollutants and reactors illuminated only during a few hours under a clear sky conditions will certainly be very useful to understand the principal features of the process, but may, on the other hand, be less appropriate for practical applications under less defined operating conditions.

2. The steady-state, continuous, tubular reactor operated with recirculation and solar irradiation

Consider a solar, continuous flow, tubular photocatalytic reactor that is operated under steady-state

conditions in a continuous flow, open, recirculating system (Fig. 1). The incoming volumetric flowrate is given by $Q_{\text{Sys}}^{\text{in}}$ ($Q_{\text{Sys}}^{\text{in}} = Q_{\text{Sys}}^{\text{out}}$) and the recirculation flowrate is Q_{Rec} . The reactor flowrate is Q_{R}^{in} . There are three important concentrations: $C_{\text{Sys}}^{\text{in}}$, $C_{\text{Sys}}^{\text{out}}$ and C_{R}^{in} because $C_{\text{R}}^{\text{out}} = C_{\text{Sys}}^{\text{out}}$. The mass balance in control volume 1 (enclosed by broken lines, cf. Fig. 1) yields:

$$Q_{\text{Sys}}^{\text{in}} (C_{\text{Sys}}^{\text{out}} - C_{\text{Sys}}^{\text{in}}) = \langle \Omega \rangle_{V_{\text{R}}} V_{\text{R}} \quad (1)$$

Ω is the reaction rate for the key component, the concentration of which is measured. For wastewaters, these concentrations are often expressed in terms of COD values. V_{R} is the only volume where a reaction takes place; i.e. the irradiated volume. $\langle \cdot \rangle_{V_{\text{R}}}$ stands for a reactor volume averaged property. In Eq. (1) the volume averaged reaction rate has been used on the account that, in general, the reaction rate is a function of the position inside V_{R} . For constant V_{R} and considering the definition of the actual Observed Photonic Efficiency (Sagawe et al., 2003a):

$$\zeta_{\text{act}}^{\text{Sys}} = \frac{dN}{\langle q \rangle_{A_{\text{inc}}} A_{\text{inc}} dt} \quad (2)$$

Eq. (1) can be rewritten as:

$$Q_{\text{Sys}}^{\text{in}} (C_{\text{Sys}}^{\text{out}} - C_{\text{Sys}}^{\text{in}}) = \zeta_{\text{act}}^{\text{Sys}} \langle q \rangle_{A_{\text{inc}}} A_{\text{inc}} \quad (3)$$

A mass balance in the control volume 2 (enclosed by dotted and broken lines, cf. yields:

$$Q_{\text{Sys}}^{\text{in}} + Q_{\text{Rec}} = Q_{\text{R}}^{\text{in}} \quad (4)$$

And

$$Q_{\text{Sys}}^{\text{in}} C_{\text{Sys}}^{\text{in}} + Q_{\text{Rec}} C_{\text{Sys}}^{\text{out}} = Q_{\text{R}}^{\text{in}} C_{\text{R}}^{\text{in}} \quad (5)$$

The assumption has been made here that the change in concentration produced by adsorption of the pollutant on the catalytic surface is negligible compared with the pollutant concentration entering the recirculating system.

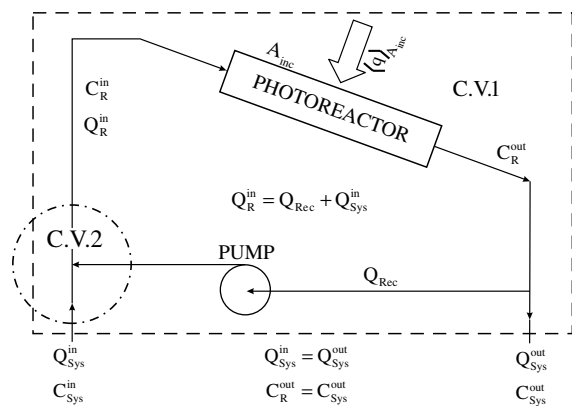


Fig. 1. Recirculating reactor.

It is known that the kinetics of many photocatalytic reactions can be phenomenologically and reasonably well represented by Langmuir–Hinshelwood type of kinetics. This formal mathematical treatment renders an expression that is a zero order rate equation for high pollutant concentrations and a first order rate law for low concentrations. In order to keep the simplicity of these derivations a conservative approach will be adopted and a first order reaction will be used throughout. Thus, the development that follows is valid for any kinetics that can be reduced, in a first approximation, to a first order kinetics. It will be further assumed that the velocity and concentration profiles in the tubular reactor are flat. These choices permit the derivation of analytical results. With these assumptions the mass balance in the tubular reactor is given by:

$$\frac{Q_{\text{R}}^{\text{in}}}{A_{\text{C}}} \frac{d\langle C_{\text{R}} \rangle_{A_{\text{C}}}}{dz} = -k C_{\text{R}} \quad (6)$$

With the boundary condition (B.C.):

$$z = 0 \quad C_{\text{R}} = C_{\text{R}}^{\text{in}} \quad (7)$$

k is a pseudo first order rate constant, that is, at least, a function of the incoming radiation flux to the reactor photon harvesting area. Integrating Eq. (6) with B.C. (7) and defining the Photocatalytic Damköhler number one as $Da_{\text{I,P}}^{\text{Stat}} = k \tau_{\text{R}} = k(V_{\text{R}}/Q_{\text{R}}^{\text{in}})$:

$$C_{\text{R}}^{\text{out}} = C_{\text{Sys}}^{\text{out}} = C_{\text{R}}^{\text{in}} \times \exp(-Da_{\text{I,P}}^{\text{Stat}}) \quad (8)$$

With τ_{R} being the tubular reactor mean residence time.

In a previous paper (Sagawe et al., 2004) it was shown that the first order kinetic constant can be written in terms of the Local Observed Photonic Efficiency and the observable variables as follows:

$$k = \frac{\zeta_0}{C_0} \frac{\langle q \rangle_{A_{\text{inc}}} A_{\text{inc}}}{V_{\text{R}}} \quad (9)$$

In the derivation of Eq. (9) the following assumptions have been made: (i) the liquid hold up is very close to unity (ii) the Photon Flux q is independent of z and (iii) as expected in modern solar photocatalytic systems, a non-light concentrating equipment is used (to collect also diffuse radiation) and, consequently, irradiation rates are low (not exceeding one sun); thus the effect of the absorbed light intensity is of first order and the photonic efficiency is independent of variations in the photon flux. These assumptions will be maintained throughout this work.

ζ_0 and C_0 are the Observed Photonic Efficiency and the concentration at some reference conditions, for example, the initial concentration of several recirculating systems in series. From Eq. (9), the Photocatalytic Damköhler number is obtained as:

$$Da_{\text{I,P}}^{\text{Stat}} = \frac{\zeta_0}{C_0} \frac{\langle q \rangle_{A_{\text{inc}}} A_{\text{inc}}}{Q_{\text{R}}^{\text{in}}} = \frac{\zeta_0}{C_0} \times PI_{\text{PFR}}^{\text{Stat}} \quad (10)$$

In Eq. (10) $PI_{\text{PFR}}^{\text{Stat}}$ is the steady-state, Photon Input to the solar reactor (Sagawe et al., 2004), i.e., the energy per unit volume that is entering the reactor in a defined wavelength range. Let us define:

$$\text{The recirculation ratio: } R = \frac{Q_{\text{Rec}}}{Q_{\text{Sys}}^{\text{in}}} \quad (11)$$

The conversion for the whole system:

$$X_{\text{Sys}} = 1 - \frac{C_{\text{Sys}}^{\text{out}}}{C_{\text{Sys}}^{\text{in}}} \quad (12)$$

The Photon Input to the total system:

$$PI_{\text{Sys}}^{\text{Stat}} = \frac{\langle q \rangle_{A_{\text{inc}}} A_{\text{inc}}}{Q_{\text{Sys}}^{\text{in}}} \quad (13)$$

The Damköhler number for the total system:

$$Da_{\text{I,P}}^{\text{Sys}} = \frac{\zeta_0}{C_0} \frac{\langle q \rangle_{A_{\text{inc}}} A_{\text{inc}}}{Q_{\text{Sys}}^{\text{in}}} \quad (14)$$

And the following relation (Sagawe et al., 2004):

$$\frac{\zeta_0}{C_0} = \frac{\zeta_x^{\text{PFR}}(z)}{C_{\text{R}}(z)} = \frac{\zeta_{\text{Sys}}^{\text{in}}}{C_{\text{Sys}}^{\text{in}}} \quad (15)$$

Eq. (15) is only valid for first order kinetics. Combining Eqs. (4), (5), (11):

$$C_{\text{R}}^{\text{in}}(1+R) = C_{\text{Sys}}^{\text{in}} + R C_{\text{Sys}}^{\text{out}} \quad (16)$$

With Eqs. (4), (8), (10), (11), (14), (16):

$$\begin{aligned} \frac{C_{\text{Sys}}^{\text{out}}}{C_{\text{Sys}}^{\text{in}}}(1+R) &= \left(1 + R \frac{C_{\text{Sys}}^{\text{out}}}{C_{\text{Sys}}^{\text{in}}}\right) \times \exp\left[-\frac{\zeta_0}{C_0} \frac{\langle q \rangle_{A_{\text{inc}}} A_{\text{inc}}}{Q_{\text{Sys}}^{\text{in}}(1+R)}\right] \\ &= \left(1 + R \frac{C_{\text{Sys}}^{\text{out}}}{C_{\text{Sys}}^{\text{in}}}\right) \times \exp\left(-\frac{Da_{\text{I,P}}^{\text{Sys}}}{1+R}\right) \end{aligned} \quad (17)$$

Using definitions (12) and (13):

$$X_{\text{Sys}} = 1 - \frac{\exp\left[-\frac{\zeta_0}{C_0} \frac{PI_{\text{Sys}}^{\text{Stat}}}{(1+R)}\right]}{1 + R \left\{1 - \exp\left[-\frac{\zeta_0}{C_0} \frac{PI_{\text{Sys}}^{\text{Stat}}}{(1+R)}\right]\right\}} \quad (18)$$

From Eq. (18) the Photocatalytic Damköhler number for the whole system is calculated as:

$$Da_{\text{I,P}}^{\text{Sys}} = \frac{\zeta_0}{C_0} PI_{\text{Sys}}^{\text{Stat}} = -\ln\left[\frac{(1+R)(1-X_{\text{Sys}})}{1+R(1-X_{\text{Sys}})}\right](1+R) \quad (19)$$

Combining Eqs. (3), (12), (13) and (19):

$$\begin{aligned} \zeta_{\text{act}}^{\text{Sys}} &= \frac{C_{\text{Sys}}^{\text{in}} X_{\text{Sys}}}{PI_{\text{Sys}}^{\text{Stat}}} = \zeta_0 \frac{C_{\text{Sys}}^{\text{in}}}{C_0} \frac{X_{\text{Sys}}}{Da_{\text{I,P}}^{\text{Sys}}} \\ &= \zeta_0 \frac{C_{\text{Sys}}^{\text{in}}}{C_0} \frac{X_{\text{Sys}}}{-\ln\left[\frac{(1+R)(1-X_{\text{Sys}})}{1+R(1-X_{\text{Sys}})}\right](1+R)} \end{aligned} \quad (20)$$

Eq. (20) provides the actual observed photonic efficiency for the recirculating system in terms of the OPE at reference conditions, i.e., the inlet concentration to the system, the conversion and the recirculation ratio.

The Process Efficiency for the recirculating system can be defined as follows:

$$\eta_{\text{act}}^{\text{Rec}} = \eta_{\text{Total}}^{\text{Rec}} = \frac{\zeta_{\text{act}}^{\text{Sys}}}{\zeta_{\text{act}}^{R=0}} \quad (21)$$

That is, an efficiency calculated with respect to a plug flow reactor without recirculation. If there were not limitations caused by the oxygen solubility or if the reactor could be operated with a continuous injection of oxygen, this would be the most efficient system. The denominator of Eq. (21) is equal to:

$$\zeta_{\text{act}}^{R=0} = \lim_{R \rightarrow 0} \zeta_{\text{act}}^{\text{Sys}} = \zeta_0 \frac{C_{\text{Sys}}^{\text{in}}}{C_0} \frac{X_{\text{Sys}}}{-\ln(1-X_{\text{Sys}})} \quad (22)$$

For a single plug flow reactor $C_{\text{Sys}}^{\text{in}} = C_0$ and the corresponding actual OPE is:

$$\zeta_{\text{act}}^{\text{PFR}} = \zeta_0 \frac{X}{-\ln(1-X)} \quad (23)$$

This Actual OPE of the plug flow reactor is equivalent to the Total OPE of a photocatalytic batch reactor (Sagawe et al., 2003a) or the Total OPE of a batch recirculating reactor with differential conversion per pass (Sagawe et al., 2004). The Process efficiency of the recirculating system can then be calculated via:

$$\eta_{\text{Total}}^{\text{Rec}} = \frac{\ln(1-X_{\text{Sys}})}{(1+R) \ln\left[\frac{(1+R)(1-X_{\text{Sys}})}{1+R(1-X_{\text{Sys}})}\right]} \quad (24)$$

The dependence of the Process Efficiency of the recirculating system on the Recirculation ratio is shown for a single reactor under different system conversions if Fig. 2 (solid lines). It can be seen that $\eta_{\text{Total}}^{\text{Rec}}$ exhibits an important dependence on the recirculation ratio and that this effect is much more significant at high conversions.

In none of these equations any restrictions of the system conversion caused by limitations in one of the key reactants (i.e., molecular oxygen) for the oxidation reaction have been included. Returning to the example discussed in the introduction, according to Eq. (16), a reactor inlet concentration of COD = 48 ppm can be reached when the system operates with 90% conversion, employing a recirculation ratio of 44. This operating point has been marked in Fig. 2 by an open square. It is evident that the process efficiency is rather low (28%). This is because the reactor operates at rather low concentrations (between 48 and 40 ppm). This difficulty can be overcome employing a stepwise operation consisting of several recirculating systems in series.

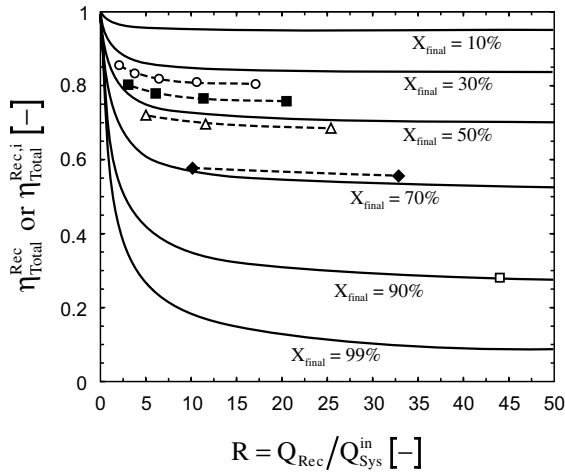


Fig. 2. Solid lines: Process efficiency as a function of the recirculation ratio for a single reactor with no limitations in the oxygen uptake. Conversion is the parameter. Symbols: \square Single reactor with recirculation and oxygen limitation, 90% conversion. \blacklozenge Same as before but with two reactors in series. \blacksquare Same as before but with three reactors in series. \blacktriangle Same as before but with four reactors in series. \circ Same as before but with five reactors in series. From $n=2$ to $n=5$ the largest process efficiency (η_i^{Rec}) corresponds to the last reactor in the series. All calculations for an incoming COD = 400 ppm (C_0) and a maximum conversion per pass of 8 ppm.

Thereby, the average operating concentration in each reactor is decreased more gradually. At its theoretical limit, i.e., with the number of stages approaching infinity, the system turns into a single, continuously aerated reactor.

3. n-Steps recirculating system

Consider the case of a series of recirculating systems as shown in Fig. 3. For each of the individual steps the following restriction apply:

$$\Delta C_i^R = (C_R^{in} - C_R^{out})_i \leq \Delta C_{max}^R \tag{25}$$

Here concentrations could be expressed in terms of COD values. At 20 °C, ΔC_{max}^R is approximately 8 ppm. Combining Eq. (16) with the restriction defined in Eq. (25) the limitation for each step becomes:

$$C_{i-1} - C_i \leq (1 + R_i)\Delta C_{max}^R \tag{26}$$

It is also known that R_i must be as low as possible since the Process Efficiency decreases as the recirculation ratio increases (cf. Fig. 2). Moreover, increasing the recirculation ratio increases the operational costs. Consequently, in addition to Eq. (26) we have the restriction that:

$$R_i = R_{min} \text{ and } R_{min} > 0 \tag{27}$$

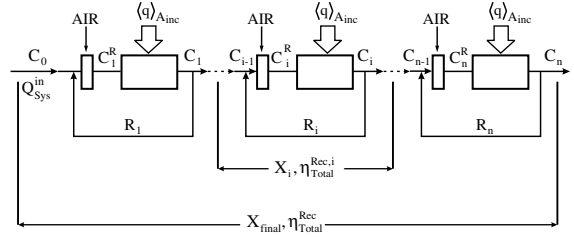


Fig. 3. System consisting of n recirculating reactors in series.

With Eqs. (12)–(14) and (18) we obtain:

$$C_i = C_{i-1} \frac{\exp\left(-\frac{Da_{i,P}^R}{1+R_i}\right)}{1 + R_i \left[1 - \exp\left(-\frac{Da_{i,P}^R}{1+R_i}\right)\right]} \tag{28}$$

In Eq. (28) we have:

$$Da_{i,P}^R = \frac{\zeta_0 \langle q_i \rangle_{Ainc,i} A_{inc,i}}{C_0 Q_{Sys}^{in}} = \underbrace{\frac{1}{n} Da_{1,P}^{Sys}}_{\text{if } n \text{ equal steps are used}} \tag{29}$$

Thus, if C_{i-1} , $Da_{i,P}^R$ and ΔC_{max}^R are known or fixed, C_i and R_i can be calculated by iteration from Eq. (28) and the restrictions given by Eqs. (26) and (27). For a n steps process (n recirculating units), if C_0 , $Da_{1,P}^{Sys}$, ΔC_{max}^R and n are known or fixed and Eq. (28) is used, the final conversion $X_{Sys} = 1 - C_n/C_0$ can be calculated for each value of n ($n = 1, 2, \dots, n$) employing a recursive methodology. Once X_{Sys} is calculated for the minimum R_i , from Eq. (20) the total OPE (equal to the actual OPE) can be calculated by:

$$\zeta_{act}^{Sys} = \zeta_{total}^{Sys} = C_0 \frac{X_{Sys}}{P_{j,Stat}^{Sys}} = \zeta_0 \frac{X_{Sys}}{Da_{1,P}^{Sys}} \tag{30}$$

It should be noted here that, in order to obtain a better information about the magnitude of the thus calculated observed photonic efficiency, the result should be compared with that of a single tubular reactor with continuous injection of air as in the case of the aerated cascade reactor mentioned previously. i.e., the process efficiency must be calculated.

It is an important result of the previously described mathematical procedure that n has to be optimized taking into account that the maximum process efficiency is obtained with $n \rightarrow \infty$ which, however leads to the maximum equipment cost. Conversely, choosing a process consisting only of a few steps leads to a low process efficiency and consequently the need for larger photon harvesting areas, which means larger photoreactors and one again higher costs. Thus, a typical design problem is apparent. Eventually, the trade-off solution will be obtained by fixing an acceptable value of the total Process Efficiency and calculating the corresponding value of n by a second iteration (this time changing n).

However, very often X_{Sys} is the fixed target and the corresponding Damköhler numbers, i.e., $Da_{i,P}^R$ and

$Da_{I,P}^{Sys}$ are needed. Since X_{Sys} is calculated in a recursive manner as explained before, in this case, an additional iteration must be applied. Thus, $Da_{I,P}^{Sys}$ is assumed and the problem is solved recursively starting from C_0 and calculating, iteratively, each step to obtain C_i from C_{i-1} with the restriction imposed by Eqs. (26) and (27). In this way C_n and X_{Sys}^{Calc} are obtained. Comparing the last result with the desired conversion, X_{Sys}^{Des} , the additional iteration can be performed until $X_{Sys}^{Calc} \cong X_{Sys}^{Des}$. The pair of values $Da_{I,P}^{Sys}$, $X_{final} = X_{Sys}^{Calc}$ can now be used to calculate the total OPE: $\zeta_{Total} = \zeta_{Total}(\zeta_0, C_0, \Delta C_{max}^R, n, X_{final}, Da_{I,P}^{Sys})$.

Hence, the process efficiency with respect to a reactor not limited by any restriction in the maximum COD conversion per pass can be calculated:

$$\eta_{act}^{Rec} = \frac{\eta_{Total}^{Rec}}{\zeta \{ \text{Calculated for the } n - \text{step recirculating system} \}} = \frac{\zeta \{ \text{Calculated for the tubular reactor with } R = 0 \}}{\zeta \{ \text{Calculated for the } n - \text{step recirculating system} \}} \quad (31)$$

Clearly, the denominator will be equal to:

$$\zeta_{act}^{PFR} = \zeta_0 \frac{X_{final}}{-\ln(1 - X_{final})} \quad (32)$$

In Eq. (32) $X_{final} = (X_R^{out})_{SinglePFR}$. Combining Eqs. (30)–(32) but now for $X_{final} = X_{Sys}^{Des}$:

$$Da_{I,P}^{Sys} = \frac{-\ln(1 - X_{final})}{\eta_{Total}^{Rec}} \quad (33)$$

and

$$Da_{I,P}^i = \frac{-\ln(1 - X_{final})}{n \times \eta_{Total}^{Rec}} \quad (34)$$

Eq. (34) can be combined with Eq. (28) to yield:

$$C_i = C_{i-1} \frac{\exp \left[\frac{\ln(1 - X_{final})}{n \times \eta_{Total}^{Rec} (1 + R_i)} \right]}{1 + R_i \left[1 - \exp \left[\frac{\ln(1 - X_{final})}{n \times \eta_{Total}^{Rec} (1 + R_i)} \right] \right]} \quad (35)$$

Based upon this equation, a new approach to solve the problem can be proposed. Suppose that C_0 and ΔC_{max}^{PFR} are known and X_{final} and n are adopted, then, the combination of iterations and recursive calculations shown in Fig. 4 yields: η_{Total}^{Rec} , all R_i and C_i for any X_{final} and n . It is once again possible to iterate with the number of units n if the obtained process efficiency η_{Total}^{Rec} is not an acceptable value.

Returning to Fig. 2 it is obvious that all black lines correspond to the values of η_{Total}^{Rec} as a function of R having the conversion X_{final} as a parameter and $n = 1$. These results do not take into account the oxygen limitation given by ΔC_{max}^R . Instead, the symbols (single values) in the Figure are a representation of $\eta_{Total}^{Rec,i}$ with the corresponding value of R_i taking into account the limitations in conversions produced by the oxygen availability. In this case the results are given for a particular example

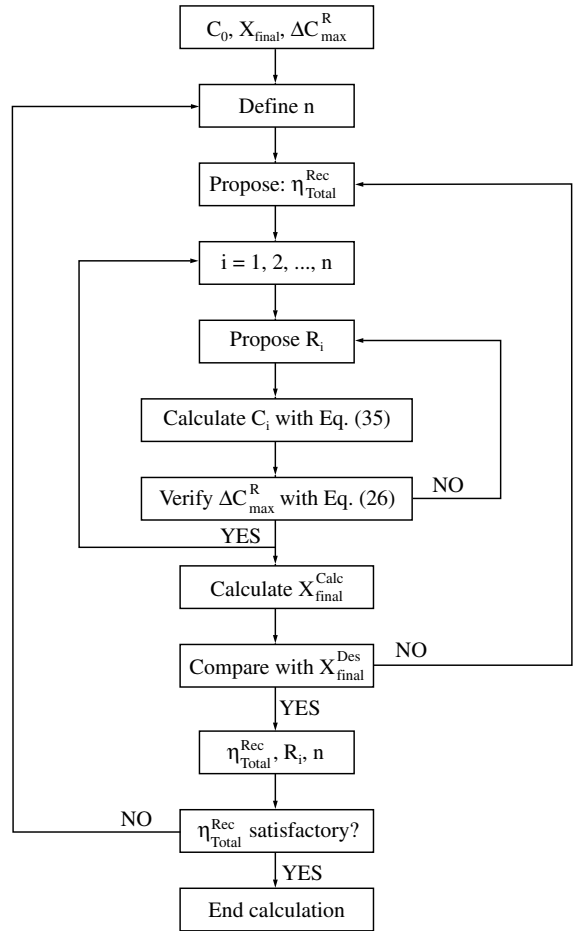


Fig. 4. Calculation procedure with Eqs. (35) and (26).

with an initial COD concentration of 400 ppm, a change in COD in each reactor equal to 8 ppm, and a total pollutant degradation of 90%. Thus, with $n = 1$, the single reactor process efficiency is 0.28 and the total system process efficiency has the same value. In the case of $n = 5$ each of the reactors with optimized R_i operates with a total process efficiency, $\eta_{Total}^{Rec,i}$, ranging from 0.804 to 0.856 resulting in a total system process efficiency for the entire $n = 5$ steps of 0.82. Table 1 summarizes values derived for the total process efficiency of the whole system when n is changed from $n = 1$ to $n = 5$.

A higher efficiency can be achieved for a higher number of steps; i.e., for an operation with 45 individually aerated plug flow reactors in series and $R = 0$. With $n \rightarrow \infty$, η_{Total}^{Rec} for the entire system approaches unity which is the same efficiency as that of a continuously aerated, single, plug flow reactor without recirculation (cf. previously quoted ACP reactor, Sagawe et al., 2001).

Fig. 5 shows a plot of η_{Total}^{Rec} as a function of $C_n/C_0 = 1 - X_{final}$ using the number of reactors in series as a parameter for $n = 1$ to $n = 5$. Note that the abscissa

Table 1
Process efficiencies as a function of the number of steps

$X_{\text{Sys}} = 0.9; C_0 = 400 \text{ ppm}; \Delta C_{\text{max}}^R = 8 \text{ ppm (Temp. = 20 }^\circ\text{C)}$

Symbol in Fig. 2	N	$\eta_{\text{Total}}^{\text{Rec}}$
○	5	0.82
■	4	0.78
△	3	0.70
◆	2	0.57
□	1	0.28

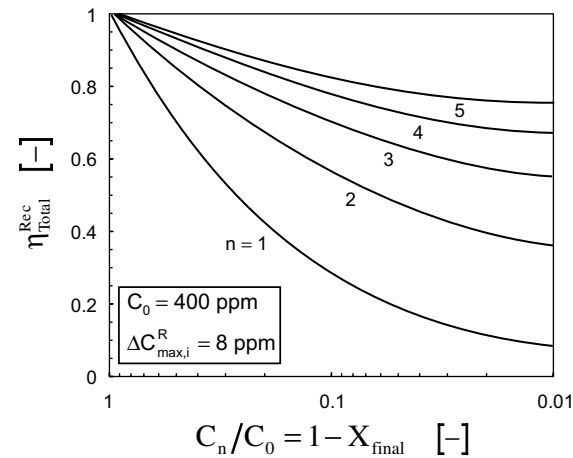


Fig. 5. Total process efficiency as a function of the dimensionless exit concentration. The number of reactor in series is the parameter.

of the figure has been drawn with a logarithmic scale. This graphic representation is valid for an initial COD concentration of 400 ppm and an allowed change of the COD concentration of 8 ppm. per pass. For an exit conversion of 0.99 and $n = 5$ the total system process efficiency is found to be very close to 80%.

For a given number of stages (n), the total efficiency can be obtained from the efficiency of each step as follows:

$$\eta_{\text{Total}}^{\text{Rec}} = \frac{1}{n} \sum_{i=1}^{i=n} \eta_i^{\text{Rec}} \quad (36)$$

In the following table, results using the iterative-recursive solution are shown for the example that has been used throughout this work.

To illustrate the influence of the initial COD concentration on the required number of stages and the recirculation ratios Table 3 shows the results of the same calculations for an initial COD = 40 ppm.

For the case of 400 ppm Table 2 suggests that the technical solution should not exceed much more than

Table 2
Calculation of Process efficiencies

Stages	Iterative-recursive solution ^a			
	X_i	C_i (ppm)	R_i	η_i^{Rec}
1	0.90	40	44	0.28
1	0.68	129.22	32.85	0.56
2	0.69	40	10.15	0.58
				0.57
1	0.36	255.22	17.10	0.80
2	0.36	162.33	10.61	0.81
3	0.37	102.74	6.45	0.82
4	0.38	64.51	3.78	0.83
5	0.38	40	2.06	0.86
				0.82
1	0.16	336.61	6.92	0.93
2	0.16	283.18	5.68	0.93
3	0.16	238.12	4.63	0.93
4	0.16	200.14	3.75	0.93
5	0.16	168.11	3.00	0.94
6	0.16	141.11	2.37	0.94
7	0.16	118.35	1.85	0.95
8	0.16	99.16	1.40	0.95
9	0.16	82.99	1.02	0.96
10	0.16	69.35	0.70	0.96
11	0.17	57.86	0.44	0.97
12	0.17	48.17	0.21	0.98
13	0.17	40	0.02	1.00
				0.95

$C_0 = 400 \text{ ppm}; X_{\text{final}} = 0.90; \Delta C_{\text{max}}^R = 8 \text{ ppm (Temp. = 20 }^\circ\text{C)}$
^a All values have been rounded to two decimal figures.

Table 3
Calculation of process efficiencies

Stages	Iterative-recursive solution ^a			
	X_i	C_i (ppm)	R_i	η_i^{Rec}
1	0.90	4.00	3.5	0.47
1	0.64	14.35	2.21	0.72
2	0.72	4.00	0.29	0.90
				0.81
1	0.50	20.03	1.50	0.82
2	0.54	9.26	0.35	0.92
3	0.57	4.00	0.00	1.00
				0.91
1	0.41	23.55	1.06	0.88
2	0.43	13.32	0.28	0.95
3	0.45	7.30	0.00	1.00
4	0.45	4.00	0.00	1.00
				0.96

$C_0 = 40 \text{ ppm}; X_{\text{final}} = 0.90; \Delta C_{\text{max}}^R = 8 \text{ ppm (Temp. = 20 }^\circ\text{C)}$
^a All values have been rounded to two decimal figures.

five reactors. It can also be observed from Tables 2 and 3 that the possibility of reaching very high total process efficiencies is inversely proportional to the requested conversion. This is a direct consequence of the first order

kinetics used in the derivation of the equations developed in this work.

4. Conclusions

Simple analytical solutions have been obtained that represent the performance of a system made of n -steps, photocatalytic, flow reactors with recirculation, accounting for the limitations produced by the maximum oxygen availability in aqueous solutions. For given initial concentrations and defined final conversions, these results allow the calculation of the process efficiency in a simple way and expedite the decision concerning the most convenient number of reactors for the solar photocatalytic water treatment system.

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