



Article Ideal Reactors as an Illustration of Solving Transport Phenomena Problems in Engineering

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Abstract: This contribution aims at emphasizing the importance of ideal reactors in the field of environmental engineering and in the education of the corresponding engineers. The exposition presents the mass flow governing equations of the ideal reactors (batch, completely mixed flow, and plug flow reactors) as particular cases derived from the integral version of the conservation of mass of a chemical/biological species. In the case of transient problems and simple kinetics, such expressions result in first-order ordinary differential equations amenable to be solved analytically when they are linear. In this article, it is shown that when they are non-linear, due to the presence of a second-order kinetics reaction, an analytical solution is also possible, a situation not dealt with in the textbooks. Finally, the previous findings are integrated into a teaching proposal addressed to help undergraduate students to solve more efficiently ideal reactor problems.

Keywords: problem-solving in engineering; ideal reactors; mass conservation integral equation; Riccati equation; second-order kinetics



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1. Introduction

Reactors play an important role in environmental science and technology. Even the Earth system (the whole ecosystem) or the biosphere can be studied as a huge reactor, or even more precisely, as a very complex bioreactor. Then, particular ecosystems such as rivers basins, lakes, and wetlands can be modeled according to the reactor theories. Thus, on the one hand, reactors are important for environmental engineers since their conceptual framework and tools are useful to model and simulate the behavior and response of particular ecosystems over anthropogenic stress. In other words, reactor theories and applications can indeed be employed in environmental impact assessment exercises, both for explaining environmental damage which has already happened or is about to happen and to forecast the environmental consequences of policies, programs, and projects.

On the other hand, as an inherent consequence of human activity when any kind of physical resource is used for any purpose, waste, in all its states and forms, is generated. An explanation for this general tendency in which the quality of physical resources dissipates into pollution while they are exploited lies in the second law of thermodynamics. Pollution is in fact a mass flow with high entropy which imposes both health risks to populations exposed and environmental damage in the receiving and assimilating environments [1]. Environmental engineering, from its earliest origins, has dealt with pollution. In many cases when the actual science and state-of-art technology cannot prevent pollution, treatment of the polluting flows, before they are discharged into the environment is required. Treatment can be regarded as one of the main fields in environmental engineering and the role of reactors in waste treatment engineering is of paramount importance. In fact, all treatments of substances oriented towards the modification or sanitation of their composition in order to render them harmless to the environment and riskless to human health, are engineered

to occur in reactors [2]. What is more, the so-called nature-based solutions (NbS) related to pollution prevention and control, can also be regarded in many cases as bioreactors [3].

In order to come to terms with the concept of a reactor and its multiple applications in environmental engineering it is required for students to begin with ideal reactors theory. Indeed, in environmental engineering academic syllabi found in universities from all continents, the ideal reactors theory is commonly dealt with in the scientific-based formation at early stages, before and as a requisite to, approaching the core environmental engineering fields. It is then compulsory for students to have developed skills in the formulation of ideal reactors as a previous step in the design of engineered solutions to environmental problems.

Usually, ideal reactors are classified into two types: continuously stirred tank reactors (CSTRs) and plug flow reactors (PFRs). In the first kind, perfect mixing is assumed; this means that the chemical species after the entry is instantaneously and uniformly mixed in the whole reactor. As a consequence, its concentration is homogeneous. CSTRs can be imagined as vessels equipped with agitators and/or heat transfer devices helping in the mixing process. If the vessel has no flow (input or output) it is called a Batch Reactor which is characterized by a non-continuous operation: after a batch has been processed, the reactor is emptied, and the next batch can be treated. If, however, the vessel has a flow through it, the reactants can be processed continually into products, and it is called a Completely Mixed Flow Reactor (CMFR). Due to the assumed perfect mixing, the concentration and temperature of the system inside is identical to that of the outgoing stream.

In the second type of ideal reactors, the flow through the reactor is modeled as succession of fluid thin slices (or plugs), each of them with uniform concentration, advancing with uniform velocity through the reactor; however, concentration changes from one plug to the neighbor, in such a way that the fluid is not mixed in the advancing direction, but it is perfectly mixed in the transversal direction. Therefore, a PFR can be conceived as a conduit where reactants enter the reactor through the inlet, undergo transformations during their transit and products emerge from the outlet. This type of reactor always operates in steady state because for a given inlet concentration, the value of the concentration *C* at a fixed location in the PFR does not vary with respect to time [4].

Given the relevance of reactors engineering in the education of environmental engineers, the purpose of this article is manifold: firstly, to present a comprehensive account of the application of the reactors in the more consolidated environmental engineering fields; secondly, to introduce the fundamentals of reactor engineering highlighting that the governing equations of the ideal reactors (batch, completely mixed flow, and plug flow reactors) should be regarded as particular cases derived from the integral version of the conservation of mass of a chemical/biological species. Since this is not always the case in the approach followed by the majority of textbooks that develop the subject, this contribution points out that for undergraduate students it is relevant to have a more accurate and general framework of reactor fundamentals. Thirdly, this work shows that when dealing with second-order kinetics reactions an analytical solution is also possible, a situation not previously contemplated in textbooks. Fourthly, a teaching approach is proposed, contrasting the conventional way textbooks deal with reactor problems, which is based on the mass balance equation. Instead of that, it is suggested here to derive the ideal reactor governing equations from the general integral transport equation of fluid mechanics, seeking to provide students with a stronger and wider conceptual framework that strengthens skills for resolving general engineering problems in which recognizing cause-effect relationships is a crucial key.

Overall, this article aims at offering a first encounter for environmental engineering students with ideal reactor fundamentals addressing that they are a particular case of general fluid mechanics mass conservation equation and showing the great applicability this conceptual framework has in a nowadays growing field. The analysis of energy flow, which also happens in ideal reactors, is out of the scope of the present contribution.

The present contribution is structured as follows: starting with a description of reactors theories and applications in different fields of environmental engineering, an approach for

dealing with such ideal reactors is described. In the first place, the governing equations are derived from the integral version of fluid mechanics conservation principles, pointing out its restrictions. Second, solutions are obtained for all cases of interest in a systematic way, avoiding tedious processes for solving problem-specific ordinary differential equations. Finally, based on the previous results, a teaching approximation is proposed aimed at helping students to efficiently analyze and solve ideal reactor problems.

2. Reactors in Environmental Engineering and Science

A reactor is an open system that operates under controlled conditions. As such it is fed by one or more inflows in which substances (in this case substances of environmental concern) are conveyed into the reactor. These substances enter the reactor through a mass flow given by the product between the concentration of the substance and the inflow. Once in the reactor, and for a determined and decisive time denoted as residence time, the substances undergo several transformations that may be of physical, chemical, or biological nature. As a result of these transformations, the substance concentrations suffer variations, giving birth to new products and byproducts. Once the residence time is over, products and byproducts are taken out from the reactor through several outflows. It has to be pointed out that the reactor is designed precisely in order to obtain the new products, while the byproducts are secondary outcomes that in many cases still require appropriate management (i.e., further treatment). Thus, while in general products are innocuous or harmless substances, byproducts can still impose unacceptable environmental risks. For a particular substance of interest (e.g., a contaminant), it is again possible to estimate the mass flow which leaves the reactor by the product between the concentration of the substance and the outflow which takes it out. Here, the difference between the mass flow entering the reactor and the mass flow leaving it, for that particular substance, becomes rather important since the removal efficiency for the contaminant obtained by the reactor can be estimated through this difference divided by the inflow mass.

Two elements determine a reactor's behavior and performance: fluid dynamics and chemical kinetics. While the residence time depends on fluid dynamics, as well as physical processes such as sedimentation or equalization, chemical, and biochemical transformations of species depend on their kinetics. Environmental engineering contaminants, which are to be treated in reactors, can follow a zero-order, a first-order, or a second-order degradation kinetics, depending on how the transformation of the substance occurs in the function of their own concentrations. Accordingly, reactors in environmental engineering practice must be designed in order to guarantee the fluid dynamics required to meet the residence time that chemical kinetics demand to render the species environmentally innocuous or human health riskless. Taking fluid dynamics and chemical kinetics into account, several types of ideal reactors can be distinguished in environmental engineering as has been pointed out previously: batch reactors and continuous reactors, as well as plug flow reactors. From these ideal reactors the so-called "reactors models" are developed, even though all actual reactors in environmental engineering differ to some extent from the ideal reactor model upon which has been designed.

From the above description, it is clear that reactors are the main device where engineered treatment processes take place. Among engineered treatment processes those related to waste treatment are of great relevance in environmental engineering. Almost every human activity dissipates energy that is able to do work and then waste (i.e., dissipated energy) is produced, bringing about pollution phenomena in water bodies, in the atmosphere, and in soils. Pollution has the potential of harming both the integrity of ecosystems and human health. The greenhouse effect, which is responsible for global warming, could be the most notorious example of the former, while morbidity and mortality associated with water-borne diseases are still nowadays a dramatic example of the latter.

Polluting flows generated by human activity can be of a very wide variety. In terms of wastewater, some of the main polluting flows are domestic wastewater, industrial wastewater, which enormously varies in function of the industrial process, agricultural run-

off, and leachate coming from landfills. Regarding solid waste, the polluting flow can be named domestic solid waste, industrial solid waste, hazardous waste, and hospital waste. Thirdly, related to air emissions, they can be classified according to their origin as mobile sources associated with transport means, stationary sources, and area sources. Atmospheric pollution flow can affect both at a global scale (e.g., global warming, ozone layer depletion, and acid rain) and at a local scale (e.g., air quality in cities). Environmental engineering solutions for dealing with all mentioned polluting flows are based on treatments, which are designed to come about in reactors.

Wastewater engineering is one of the most developed fields in environmental engineering. The developments in wastewater treatment in the last 100 years or so, have been possible in accordance with the accuracy and polishing of the models which represent the hydraulics of the reactors as well as the chemical and biochemical reactions that take place inside. Almost all unit operations in wastewater treatment plants are reactors: (a) pretreatment unit operations such as screening, comminution, sedimentation for grit removal, skimming, and flow equalization; (b) primary treatment unit operations such as sedimentation and flotation; (c) secondary treatment unit operations such as biological processes (aerobic or anaerobic); (d) tertiary treatment unit operations such as filtration, air stripping, adsorption, ion exchange, chemical precipitation, chemical oxidation, and disinfection processes including chlorination, ozonation or UV irradiation [5–8]. While in the pretreatment and primary treatment unit operations, the driving forces inside the reactors are physical whose purpose is mainly to separate suspended solids from water [9,10], in the secondary treatment the reactors are designed to guarantee the best conditions for biological treatment (i.e., organic matter oxidation, nitrification, and denitrification). Reactors designed for secondary treatment must optimize the contact between the substrate (i.e., the substance which has to be treated to render it harmless to the environment) and the microorganisms which carry out the biochemical processes. The more efficient the contact between substrate and microorganisms, the shorter hydraulic residence time is required in the reactor [11]. This is a key factor since the needed hydraulic residence time in the reactor for removing a particular contaminant determines the size of the reactor and, in consequence, the required area. Finally, since tertiary treatment is a polishing step in which different treatment goals are sought, reactors can be both physical or biochemical characteristics or even only chemical as in the case of chemical oxidation or chemical precipitation.

It has to be highlighted that the so-called natural methods or technologies to treat wastewater also operate under the reactor model scheme. Treatment ponds, which can be anaerobic, facultative, or maturation ponds, are reactors with high hydraulic residence time given the extensive principle that outline these treatment technologies [12]. The same statement is true for constructed treatment wetlands in all their versions. Treatment constructed wetlands are reactors that operate under saturated conditions in a subsurface flow. Treatment subsurface constructed wetlands can be horizontal or vertical. The horizontal subsurface treatment wetlands are suitable for treating organic matter while the vertical ones are mostly employed for nitrogen removal given the alternation of aerobic-anaerobic conditions that they provide [13]. Both treatment ponds and constructed wetlands are reactors in which physical and biochemical mechanisms simultaneously take place [14]. While treatment ponds can be designed for primary, secondary, and tertiary treatment, constructed wetlands are usually implemented for nutrient removal or for further natural organic matter polishing.

The byproducts of wastewater treatment usually require treatment. The most relevant byproduct of wastewater treatment, for the environmental risks it can cause, is sludge. In fact, sludge management can represent a significant item in the wastewater treatment plan operational costs. In general, sludge produced in wastewater treatment can be classified as primary and secondary sludge [9]. Whereas primary sludge is produced by processes such as sedimentation whether with previous coagulation and flocculation or not, and clarification, secondary sludge, or bio-solids as it is often referred to, is produced as a consequence of bacterial activity when organic matter is oxidized. For both cases, reactors are needed in order to minimize the potential harmfulness of sludge. Reactors then are designed having in mind two purposes: first, to mineralize the sludge so that it becomes inert from a microbiological point of view, and to sanitize the bio-solids so that pathogenic organisms are eliminated [15].

In the field of solid waste management, reactors also are of great importance regarding treatment and final disposal. Treatment of solid waste can be carried out through mechanical, thermal, and biological methods, and it has a manifold purpose. Firstly, to get rid of undesirable waste from cities and urban centers and to reduce volumes; secondly, to minimize environmental impacts and health risks; and thirdly, and more recently, to contribute to the circular economy. In fact, material and energy recovery are key strategies in a circular economy scheme. On the one hand, in terms of materials recovery, even a recycling facility operates as a reactor in which an inflow of mixed materials with low recovery potential enters, and several outflows of separated fractions represent the reactor products. On the other hand, "from waste to energy" concepts and implementations have been gaining relevance given their evident advantages since different types of energy (e.g., electrical energy, biofuels) can be obtained from undesirable waste [16]. Pursuing such a purpose, thermal treatment as well as some kinds of biological treatment can be employed through reactors.

Regarding biological methods, two kinds of technologies are the most employed: composting and anaerobic digestion. Composting is an aerobic process that can be modeled as a bioreactor in which oxygen supply determines the sort of reactor (i.e., passive or active oxygenation), while an anaerobic digester is a bioreactor in which the inflow is organic waste, and the product outflow is stabilized organic matter [17]. In this case, methane is an important byproduct that is generally used to recover energy.

In terms of final disposal, landfill is the technological option most world widely used, regarding municipal solid waste (MSW). A landfill operates also as a bioreactor and must be designed in accordance. The bioreactor inflow is the MSW which has been collected in cites and transported to the landfill. In the majority of cases all around the world the MSW inflow feeding landfills has not been treated with any of the technological options mentioned, whereas organic matter is the main component of its composition. Food waste is at the origin of this organic matter and thus inside the landfill bioreactor an anaerobic biological oxidation of organic matter takes place. Every single landfill cell in which waste is disposed of can be seen as an anaerobic bioreactor. The final product of the landfill reactor is stabilized on mineralized organic matter, but this process can indeed take several decades [18,19]. On the other hand, byproducts of the landfill bioreactor are of the highest environmental importance as they are the bioreactor outflows and have a high pollution potential. These outflows are biogas and leachate. While biogas is composed mainly of methane and carbon dioxide, which are greenhouse gases, leachate is a very concentrated wastewater with high concentrations of organic matter and ammoniacal nitrogen among others. In both cases, treatment is compulsive and again the available technological options are associated with different kinds of reactors.

Apart from waste treatment, and all its versions, reactor models can also be employed in modeling systems on a larger scale. To some extent, a control volume, used for understanding and modeling the transport and fate of contaminants in environmental engineering, can be equated to an ideal reactor. A polluting city, a polluted river, or a threatened wetland may be studied as reactors from an environmental impact assessment perspective [20–22]. Having in mind that an environmental impact associated with a particular parameter or variable, such as dissolved oxygen in a river or benzene concentration in the air, is a difference between the value of the variable of interest in a determined time and the value of the variable in the baseline or value of reference, reactor models may be useful in both calculations. Thus, in the context of an environmental impact assessment exercise, reactor models can be employed, firstly, to establish the baseline for variables of interest that are expected to undergo negative or positive transformations as a consequence of the implementation of a given program or project, and secondly, to estimate the value of

the negative or positive expected transformations in the variables. A well-known example of this application of reactor models is the case of river pollution brought about by organic matter. The very famous equation of Streeter and Phelps (1925) [23] is derived from modeling a river as a plug flow reactor. The application of the Streeter and Phelps model has been extensive worldwide, and almost all modern and newer water quality river models are derived from this initial approach [24,25].

As it was pointed out, before dealing with the possible applications of reactors in the environmental engineering cases mentioned in this section, students need to understand the theory of ideal reactors, since all models developed to represent such cases are built upon this theory. In the following sections, the general theory of ideal reactors is presented and our contribution to a novel approach to deal with ideal reactor teaching in environmental engineering is developed.

3. Governing Equations of Ideal Reactors

Usually, ideal reactors, namely batch, completely mixed flow (CMFR), and plug flow (PFR), are introduced in the textbooks as examples of mass conservation of chemical species. The corresponding equations are derived from scratch applying a specific mass balance for each reactor type (e.g., [4]).

Here, we propose a unified approach starting from the general integral equations obtained after applying the Reynolds Transport Theorem to the basic conservation principles. For our purposes, we start from the integral equation written for the mass concentration of a chemical species *C* with dimensions mass over volume (M L⁻³) [26]:

$$\frac{d}{dt} \int_{CV(t)} C \, dV + \oint_{CS(t)} C(\vec{v} - \vec{v}_c) \cdot \vec{n} \, da = \oint_{CS(t)} J_d da + \int_{CV(t)} r \, dV \tag{1}$$

Such an equation is written for a general control volume, CV(t), with boundary CS(t) which experiences a motion described by a velocity \vec{v}_c . In Equation (1), \vec{v} represents the fluid velocity, \vec{n} the unit normal outer to the control volume, J_d is the diffusive transport through the control volume boundary and r represents the generation or sink of mass concentration due to chemical reactions.

Conditions in which ideal reactors are analyzed in this contribution are the following:

- 1. The *CV* is taken as the reactor volume which is fixed without motion or shape change $(\vec{v}_c = 0)$.
- 2. Chemical reaction is homogeneous, therefore r = r(C).
- 3. Diffusion is very small and hence negligible compared with other processes, $J_d \approx 0$.

Under these circumstances the integral Equation (1) is expressed as:

$$\frac{d}{dt} \int_{CV} C \, dV + \oint_{CS} C \, \overrightarrow{v} \cdot \overrightarrow{n} \, da = \int_{CV} r(C) \, dV \tag{2}$$

which is valid for the three types of ideal reactors considered. Equation (2) is interpreted as follows: the change in chemical species mass in the CV plus the mass entrance or exit through the CV boundaries equals the generation or consumption of mass due to chemical reactions inside the CV. The second term on the left-hand side is usually known as ingestion.

3.1. Plug Flow Reactor

As mentioned previously, the PFR operates in a steady state. Therefore, the governing equation, Equation (2) reads:

$$\int_{CV} r(C) \, dV = \oint_{CS} C \, \overrightarrow{v} \cdot \overrightarrow{n} \, da = \int_{CV} \nabla \cdot (C \, \overrightarrow{v}) \, dV \tag{3}$$

The last equality arises from the application of the Gauss theorem. Expression (3) establishes that the reaction along the reactor is equal to the ingestion. As such equality holds whatever the CV is, the integrands must be identical; therefore,

$$\nabla \cdot (C \ \overrightarrow{v}) = r(C)$$

On the other hand, the assumption of complete mixing in the transversal direction renders the flow in a PFR one-dimensional (i.e., the flow progress in the *x* direction) which translates into

$$U\frac{dC}{dx} = r(C)$$

Because the divergence operator in 1D equals the derivative respect to x and the fluid velocity is a constant value U. In this situation, the time that the species needs to spend within the reactor to reach the location x is given by $\tau = x/U$. Consequently, the former expression can be cast into the form

$$U\frac{dC}{dx} = r(C) \to \frac{dC}{d\tau} = r(C)$$
(4)

Equation (4) constitutes the equation that determines the concentration of the species $C(\tau) = C(x/U)$ inside the PFR. For solving such a differential equation, the right-hand side (RHS) reaction term needs to be specified.

3.2. Continuously Stirred Tank Reactor

In CSTRs, all the terms in Equation (2) need to be taken into account. However, as complete mixing is assumed, each individual term can be further simplified.

Owing to the homogeneity of the concentration, the unsteady term is written as:

$$\frac{d}{dt} \int_{CV} C \, dV = V \frac{dC}{dt} \tag{5}$$

Here, *V* is the total volume of the reactor.

If the reactor has several one-dimensional flow inlets and outlets, the ingestion term is evaluated as [26]:

$$\oint_{CS} C \overrightarrow{v} \cdot \overrightarrow{n} \, da = \sum_{out} C_{out} Q_{out} - \sum_{in} C_{in} Q_{in} = CQ - \sum_{in} C_{in} Q_{in} \tag{6}$$

In Equation (6) Q_x represents the volumetric flow through each individual inlet or outlet. Because of the complete mixing, the concentration at every outlet is identical to that within the reactor; as a consequence, the mass flow of species exiting the vessel is computed as *C Q*, where *Q* is the volumetric flow through the reactor.

Finally, the reaction term can be written as:

$$\int_{CV} r(C) \, dV = r(C) \, V \tag{7}$$

Collecting the previous expressions, the general differential equation satisfied by a CSTR is found:

$$\frac{dC}{dt} = r(C) + \frac{1}{V} \left[\sum_{in} C_{in} Q_{in} - CQ \right]$$
(8)

Equation (8) will be in the following employed in the description of CMFRs. In the case of a batch reactor, there is no flow so, in this case, its governing equation is

$$\frac{dC}{dt} = r(C) \tag{9}$$

Expression, which is formally identical to that of the PFR, Equation (4), with the difference that *t* means the real treatment time in the batch reactor and τ represents the transit time of the species in the PFR. This fact means that their solutions will be the same just changing $t \rightarrow \tau = x/U$.

3.3. Usual Reactions in Environmental Engineering Reactors

To be solved, the governing equations of the ideal reactors, Equations (4) and (8), need the specification of the reaction (chemical or biological) or the absence of it. Usually, simple reactions of order zero, one, or two are considered [4,27], regarding the number in the exponent of the concentration C.

Zero order: $r(C) = -k_0$ First order: $r(C) = -k_1C$ Second order: $r(C) = -2k_2C^2$

It needs to be emphasized that only simple kinetics is considered in the present contribution because they are amenable to analytical solutions. General kinetics will lead to systems of ordinary differential equations, ODESs, that have to be solved numerically.

In the former definitions k_i , i = 0, 1, 2 are the reaction constants whose dimensions depend on the reaction order. In addition, generation terms can be considered together with the former consumption reactions, usually in a combination generation–depletion of mass species. With such functional relations for the reaction contribution, the ideal reactors governing equations are ready to be solved.

4. General Solutions for Ideal Reactors

In the case of the batch reactor, the solution of the resulting differential equations from Equation (9) for the different reaction orders are easily found by direct integration and are listed in Table 1.

Reaction $r(C)$	Solution $C(t)$	
$-k_0$	$\begin{array}{ccc} C_0 - k_0 t & t \leq \frac{C_0}{k_0} \\ 0 & t > \frac{C_0}{t} \end{array}$	(10)
$-k_1C \\ -2k_2C^2$	$\frac{C_0 e^{-k_1 t}}{\frac{C_0}{1+2k_2C_0 t}}$	(11) (12)

Table 1. Solutions for the concentration C(t) in the batch reactor for the different reaction orders.

In Table 1, C_0 stands for the initial concentration in the reactor at the reference time t = 0.

In the case of PFR, Equation (4) is formally identical to Equation (9); therefore, the solutions are the same with the changes $t \rightarrow \tau = x/U$ and $C_0 \rightarrow C_{in}$, where C_{in} stands for the concentration at PFR inlet. On the other hand, engineers are mainly interested in knowing the concentration at the outlet of the reactor, i.e., at x = L. In this case, we have

$$\frac{L}{U} \times \frac{A}{A} = \frac{V}{Q}; \quad \Theta = \frac{V}{Q}$$
(13)

where *A* is the reactor transversal area. The time Θ is known as the hydraulic retention time. Finally, the solutions for the concentration al the PFR outlet are written in Table 2.

Reaction <i>r</i> (<i>C</i>)	Solution $C(L)$	
$-k_{0}$	$C_{in} - k_0 \Theta \Theta \leq rac{C_{in}}{k_0} \ 0 \Theta > rac{C_{in}}{k_c}$	(14)
$\frac{-k_1C}{-2k_2C^2}$	$\frac{C_{in}e^{-k_1\Theta}}{\frac{C_{in}}{1+2k_2C_{in}\Theta}} \overset{\kappa_0}{\to}$	(15) (16)

Table 2. Solutions for the outlet concentration C(L) in the PFR for the different reaction orders.

In the case of the solutions of Equation (8) for the CMFR, they are more elaborate as such reactors can operate in both steady and transient modes. The first step is to rewrite Equation (8) in terms of the reactor hydraulic retention time $\Theta = V/Q$.

$$\frac{dC}{dt} = r(C) - \frac{1}{\Theta}C + \frac{1}{V}\sum_{in}C_{in}Q_{in}$$
(17)

In the steady operation, Equation (17) becomes an algebraic equation that can be solved easily for all the reactive cases including that where no reaction takes place. The corresponding steady solutions, C_{∞} , are shown in Table 3.

Table 3. Solutions for the steady outlet concentration C_{∞} in the CMFR for the different reaction orders.

Reaction $r(C)$	Solution C_{∞}	
0	$\frac{1}{Q}\sum_{i=1}^{n}C_{in}Q_{in}$	(18)
$-k_0$	$\frac{1}{Q}\sum_{in}C_{in}Q_{in}-k_0\Theta$	(19)
$-k_1C$	$\frac{1}{Q} \frac{\sum_{in} C_{in} Q_{in}}{1 + k_1 \Theta}$	(20)
$-2k_2C^2$	$\frac{-1+\sqrt{1+8k_2\Theta(\sum_{in}C_{in}Q_{in})/Q}}{4k_2\Theta}$	(21)

In the case of transient operation, C(t) comes from the solution of the ordinarily differential equation (ODE) given by Equation (17). For the no reactive case and reactions of zero and first order, the resulting ordinary differential equation is linear with constant coefficients (due to the assumption of complete mixing); therefore, it can be solved by standard methods. However, here we take a different point of view: instead of solving the equations case by case, as is usually performed in standard textbooks, we will write the general solution of Equation (17), and then the specific solution will be obtained by particularizing the general solution. For that, we write Equation (17) in the canonical form

$$\frac{dC}{dt} + AC = B \tag{22}$$

whose general solution is written as [28]:

$$C(t) = C_0 e^{-At} + \frac{B}{A} \left[1 - e^{-At} \right]$$
(23)

where for the different reactions, coefficients *A* and *B* adopt the expressions shown in Table 4.

Such coefficients, plugged in the general solution Equation (23), provide the specific solution sought. In the same way, if the reactive term is a combination of terms with zeroand first-order reactions (e.g., competing processes of generation and consumption), the general solution is written in the same form, Equation (23), where coefficients *A* and *B* have to be adapted to the particular case after comparing the proper differential equation with the canonical form Equation (22). The presented approach provides an alternative method to construct the solution to ideal reactor problems in the undergraduate studies of chemical and environmental

Table 4. Coefficients A and B in the linear differential Equation (22) for each reaction case.

engineering. It is illustrated in the following example.

Reaction <i>r</i> (<i>C</i>)	Coefficient A	Coefficient B
0	$\frac{1}{\Theta}$	$\frac{1}{\nabla}\sum_{in}C_{in}Q_{in}$
$-k_0$	$\frac{1}{\Theta}$	$-k_0 + \frac{1}{\nabla} \sum_{i} C_{in} Q_{in}$
$-k_1C$	$k_1 + \frac{1}{\Theta}$	$\frac{1}{\nabla}\sum_{in}C_{in}Q_{in}$

Example 1

A certain reactor of volume 10 m³ receives a wastewater stream of 1000 L/day containing a pathogen which needs to be controlled. Such a pathogen reproduces itself at a constant rate $R_0 = 1.5$ mg L⁻¹ day⁻¹ but it is treated with a chemical using a first-order reaction of constant k = 0.12 day⁻¹. The pathogen initial concentration in the reactor is 10 mg/L and the pathogen inlet concentration is 100 mg/L. Find the pathogen concentration in mg/L after five days assuming complete mixing.

Solution

As complete mixing is assumed, the reactor in question must be a CMFR working in a transient state. As the reactor has a balanced volumetric flow, the governing ODE of Equation (17) is cast as:

$$\frac{dC}{dt} = r(C) - \frac{1}{\Theta}C + \frac{1}{\Theta}C_{in}$$

where $\Theta = V/Q$ is the reactor hydraulic retention time. Now, as the pathogen grows at a rate R_0 and is treated with a first-order reaction, the source term is written as:

$$r(C) = R_0 - kC$$

Additionally, plugging it in the ODE

$$\frac{dC}{dt} = R_0 - kC - \frac{1}{\Theta}C + \frac{1}{\Theta}C_{in}$$

Which can be expressed as:

$$\frac{dC}{dt} + (k + \frac{1}{\Theta})C = R_0 + \frac{1}{\Theta}C_{in}$$

Comparing the last expression with the canonical first order linear ODE Equation (22): $\frac{dC}{dt} + AC = B$, the coefficients are identified as:

$$A = k + \frac{1}{\Theta}; \qquad B = R_0 + \frac{1}{\Theta}C_{in}$$

The solution for the pathogen concentration is found by Equation (23)

$$C(t) = C_0 e^{-At} + \frac{B}{A} \left[1 - e^{-At} \right] = C_0 e^{-(k + \frac{1}{\Theta})t} + \frac{R_0 + \frac{1}{\Theta}C_{in}}{k + \frac{1}{\Theta}} \left[1 - e^{-(k + \frac{1}{\Theta})t} \right]$$

The reactor hydraulic retention time is $\Theta = \frac{V}{O} = 10 \, day$, and the coefficients

$$A = k + \frac{1}{\Theta} = 0.12 + \frac{1}{10} = 0.22 \text{ day}^{-1}; \quad B = R_0 + \frac{1}{\Theta}C_{in} = 1.5 + \frac{1}{10} \ 100 = 11.5 \text{ mg L}^{-1}\text{day}^{-1}$$

Plugging such values and solving, it is obtained

$$C(5 \, day) = 10 \, e^{-0.22 \times 5} + \frac{11.5}{0.22} \Big[1 - e^{-0.22 \times 5} \Big] \approx 35 \frac{\text{mg}}{\text{L}}$$

The former cases have dealt with linear differential equations whose solution have been known since a long time ago. However, in the situation that the reaction term contains a quadratic addend, Equation (17) becomes non-linear. These problems are not dealt with in the textbooks, possibly because they cannot always be analytically solved and a numerical solution has to be sought.

In the following, we show how Equation (17) in combination with a second-order reaction can be solved analytically in the CMFR with negligible diffusion. Therefore, Equation (17) is cast into the form:

$$\frac{dC}{dt} = -2k_2C^2 - \frac{1}{\Theta}C + \frac{1}{V}\sum_{in}C_{in}Q_{in}$$
(24)

which is a first-order quadratic differential equation with constant coefficients. Let us observe that the right-hand side (RHS) is actually a second-degree polynomial in the concentration *C*.

Equation (24) is a non-linear ODE that belongs to a particular type known as the Riccati equation [29]. It is expressed in canonical form as:

$$\frac{dC}{dt} = A(t)C^2 + B(t)C + D(t)$$
(25)

where the coefficients *A*, *B*, *D* could depend on the independent variable, in this case, *t*. The solution of the Riccati equation cannot, in general, be written analytically. However, in the case of ideal reactors, the coefficients are constant and the particular solution (obtained equating to zero the RHS of Equation (25)) is just the steady state solution. In this case, an analytical solution is devised in Appendix A (Equation (A6)) and it is written as:

$$C(t) = C_p + \left[\frac{1}{C_0 - C_p}e^{-(B + 2AC_p)t} - \frac{A}{B + 2AC_p}\left[1 - e^{-(B + 2AC_p)t}\right]\right]^{-1}$$
(26)

In Equation (26) C_p is the steady state solution, i.e., the particular solution of the Riccati ODE which is the standard solution of a quadratic algebraic equation,

$$C_p = \frac{-B - \sqrt{B^2 - 4AD}}{2A} \tag{27}$$

The minus sign in front of the square root guarantees $C_p \ge 0$, which is the physical solution. Of course, the solution (25) exists if only if $B^2 - 4AD \ge 0$, a fact guaranteed by the appearance of the second-order reaction (A < 0) and the incoming species mass flow (D > 0).

In the case of the CMFR with second-order reaction, Equation (24), the coefficient values are:

$$A = -2k < 0; \ B = -\frac{1}{\Theta} < 0; \ D = \frac{1}{V} \sum_{in} Q_{in} C_{in} > 0$$
(28)

where C_p is given by Equation (21), which completes the solution of Equation (27). Of course, this process is applicable to any combination of reaction order up to the second in which the restrictions A < 0, B < 0, and D > 0 are fulfilled.

Example 2

A treatment pond is used to treat an industrial waste product using a reaction that destroys the pollutant according to second-order kinetics with constant $k = 0.02 \text{ Lmg}^{-1} \text{day}^{-1}$. The pond volume is 50,000 ft³, the volumetric flow rate of the single inlet and exit is 250 ft³/h, and the inlet pollutant concentration is 80 mg/L. If the initial concentration in the pond is 50 mg/L, find the time needed for reducing 50% such initial value assuming complete mixing in the pond.

Solution

As a complete mixing is assumed, the pond must operate as a CMFR working in a transient state coupled with a second-order reaction. Therefore, the governing ODE of the pond is non-linear and should be described by Equation (24), which can be cast in the form:

$$\frac{dC}{dt} = -2kC^2 + \frac{1}{\Theta}(C_{in} - C)$$

Because there is only one inlet and exit. Comparing it with the canonical Riccati ODE Equation (25), the particular coefficients of this problem are identified

$$A = -2k;$$
 $B = -\frac{1}{\Theta};$ $D = \frac{1}{\Theta}C_{in}$

Yet 250 ft³/h × 24 h/day = 6000 ft³/day. Therefore, the pond hydraulic retention time is:

$$\Theta = \frac{V}{Q} = \frac{50,000}{6000} = 8.33 \text{ day}$$

Substituting the corresponding values, it is obtained $A = -0.04 \text{ Lmg}^{-1} \text{ day}^{-1}$, $B = -0.12 \text{ day}^{-1}$; $D = 9.6 \text{ mg L}^{-1} \text{ day}^{-1}$. With them the steady state concentration is computed by Equation (27), which by direct substitution gives $C_p = 14.06 \text{ mg/L}$.

The solution of the differential equation is that of Equation (26); the argument in the exponential is

$$B + 2AC_v = -0.12 - 2 \times 0.04 \times 14.06 = -1.24 \, day^{-1}$$

Therefore, the pollutant concentration in the pond evolves as

$$C(t) = C_p + \left[\frac{1}{C_0 - C_p}e^{-(B + 2AC_p)t} - \frac{A}{B + 2AC_p}\left[1 - e^{-(B + 2AC_p)t}\right]\right]^{-1}$$
$$C(t) = 14.06 + \left[\frac{1}{50 - 14.06}e^{1.24t} - \frac{(-0.04)}{(-1.24)}\left[1 - e^{1.24t}\right]\right]^{-1}$$
$$C(t) = 14.06 + (-0.032 + 0.060e^{1.24t})^{-1}$$

Finally, the time needed for having $C = C_0/2 = 25 \text{ mg/L}$ in the pond is obtained by solving the exponential equation

$$25 = 14.06 + (-0.032 + 0.06e^{1.24t})^{-1}$$
$$(25 - 14.06)^{-1} = -0.032 + 0.06e^{1.24t}$$
$$0.123 = 0.06e^{1.24t} \rightarrow t = \frac{1}{1.24} \ln \frac{0.123}{0.06}$$

Therefore, $t \approx 0.58 \text{ day} \approx 13.9 \text{ h}$.

5. Outline of the Teaching Proposal

As already mentioned, ideal reactors (batch, CMFR, and PFR), are introduced in nowadays standard textbooks as examples of mass conservation of a substance whose governing equations are obtained by applying a specific mass balance for each reactor type (e.g., [4,30,31]).

The specific approach recommended in those standard textbooks is the following (text extracted literally from [4]):

- 1. Draw a schematic diagram of the situation and identify the control volume and all influent and effluent flow. All mass flows that are known or are to be calculated must cross the control volume boundary.
- 2. Write the mass balance equation in general form

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{rxn}$$

- 3. Determine whether the problem is steady state (dm/dt = 0) or non-steady state (dm/dt = VdC/dt).
- 4. Determine whether the compound being balanced is conservative ($m_{rxn} = 0$) or nonconservative (m_{rxn} must be determined based on the reaction kinetics as Vr(C)).
- 5. Replace $m_{in} = Q_{in}C_{in}$ and $m_{out} = Q_{out}C_{out}$ with known or required values.
- 6. Finally, solve the problem. This will require a solution of a differential equation in non-steady problems and the solution of an algebraic equation in steady-state problems.

After these indications, a series of problems are presented in the textbook [4] where the first, shorter part is devoted to establishing the specific ODE and the second part, the longest, to solve it. Typically, in non-steady cases, the ODE is solved case by case. This approach is commonly employed in other recent textbooks (e.g., [30,31]). An exception is the less recent Nazaroff and Alvarez-Cohen (2001) [27] which has an appendix devoted to the solution of linear ODEs with constant coefficients; however, many examples still solve the differential equation for each problem, and nothing is said about Riccati-type ODEs.

In this contribution, firstly we propose to present the ideal reactors governing equations not as isolated entities but derived as particular cases of the mass conservation equation for a chemical/biological species connected with the general integral transport equation of the fluid mechanics, Equation (1), which is developed from first principles. This approach has the advantage of presenting ideal reactors as a particular application of a general theoretical framework instead of a specific problem to be dealt with in environmental engineering without an obvious connection with previous subjects learned by the students. Moreover, in the proposed approach, it is clear why the different terms of the conservation equation are evaluated in the way they are, without resorting to "recipe" or "effective" expressions that students have to apply more or less blindly. In this manner, we expect to contribute to a more comprehensive understanding of how complex processes can be properly modeled through reactor fundamentals which have been directly derived from the governing fluid mechanic mass conservation equation. These more solid scientific bases should help students in learning how to propose more suitable and sustainable engineering solutions.

In the second place, along with this contribution, we have developed solutions for the ideal reactors experiencing reactions up to the second order. Such expressions have been written as analytical general solutions of either a linear ODE or a Riccati ODE, which are valid for constant coefficients. Additionally, the restrictions needed for the existence of such solutions have been provided. Therefore, upon obtaining the differential equation that governs the ideal reactor in the specific problem to be solved by the student, the solution of such ODE can be directly written after identifying the coefficients in the corresponding canonical ODE with the actual value of variables playing a role in the problem.

The present approximation to solve the resulting ODE is helpful for students to reach the correct final problem solution allowing them to focus on its analysis. It is known that nowadays undergraduate engineering students present difficulties in solving analytically differential equations; actually, one of the main obstacles for them to solve correctly an ideal reactor problem occurs at solving the ODE. Therefore, under our proposal, once the ODE has been correctly posed, solving it requires: 1. its comparison with the canonical equation, 2. coefficient identification, and 3. substitution of their numerical values in the general solution. We believe that this method will help the students to more efficiently analyze and solve the ideal reactor problems.

6. Summary and Conclusions

The present article has discussed the relevance of ideal reactors in environmental engineering and their importance in the formation of related engineers at the first stages of their studies. Concretely, their governing equations have been obtained as particular cases of the integral mass conservation principle of fluid mechanics transcending the traditional textbooks approach in which a separate mass balance is formulated for each reactor type. In this way, students can appreciate the connection among different subjects of their engineering curriculum instead of perceiving them as separate entities. Additionally, transient solutions of the various reactors are approached from a unified perspective: the resulting first-order ODE, either linear or non-linear, can be analytically solved and a general solution is written in terms of certain constant coefficients. Such coefficients are determined by comparing the problem-specific ODE with the canonical expression; therefore, upon computing the values of such coefficients, the solution for the time-dependent concentration C(t) is readily written without the need of solving separately the corresponding ODE. As a result, the most tedious part of reactor problems which is the resolution of the differential equation is greatly simplified allowing students to focus on solution analysis. Finally, these facts have been integrated into a teaching proposal of ideal reactors for undergraduate environmental engineers addressed to help them in the analysis and effective computation of such reactors.

As the last comment, when more complex reactor problems are faced, considering several species and more general kinetics, the resulting system of ODEs may be required to be solved by numerical methods [32] as it is customary in Engineering practice [33,34].

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Appendix A. Solution of Riccati Equation with Constant Coefficients

Here, we expose the main steps for obtaining the solution of the transient CMFR with second-order reaction shown in Equation (26). We start from Equation (25) with constant coefficients

$$\frac{dC}{dt} = A'C^2 + B'C + D' \tag{A1}$$

The general solution of Equation (A1) is written as a sum of the particular (steady) solution C_p of the ODE plus a transient contribution which goes to zero as $t \to \infty$.

$$C(t) = C_p + Z(t)^{-1}$$
 (A2)

Of course, C_p is determined by Equation (27) with the restrictions A' < 0 and D' > 0. With the decomposition of Equation (A2), it is easy to see that Z(t) satisfies the linear first-order ODE [29]

$$\frac{dZ}{dt} + (B' + 2A'C_p)Z = -A' \tag{A3}$$

Comparing Equation (A3) with canonical Equation (22), identifying $A = B' + 2A'C_p$ and B = -A', solution of Equation (A3) can be written in the form (23) as:

$$Z(t) = Z_0 e^{-(B'+2A'C_p)t} - \frac{A'}{B'+2A'C_p} \left[1 - e^{-(B'+2A'C_p)t}\right]$$
(A4)

In Equation (A4), $Z_0 = Z(t = 0)$, which is computed from C_0 from Equation (A2):

$$C_0 = C_p + Z_0^{-1} \to Z_0 = \frac{1}{C_0 - C_p}$$
 (A5)

Finally, including Equation (A5) in Equation (A4) and the result in Equation (A2), the analytical solution of the Riccati ODE, Equation (A1) is written as:

$$C(t) = C_p + \left[\frac{1}{C_0 - C_p}e^{-(B' + 2A'C_p)t} - \frac{A'}{B' + 2A'C_p}\left[1 - e^{-(B' + 2A'C_p)t}\right]\right]^{-1}$$
(A6)

In solution Equation (A6), $Z(t \to \infty)^{-1} = 0$ if $B' + 2A'C_p < 0$, which in the CMFR problem with second-order reaction is guaranteed by Equation (28).

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