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Review

Sequential chemical–biological processes for the treatment of industrial wastewaters: Review of recent progresses and critical assessment

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HIGHLIGHTS

- Sequential treatment has been demonstrated at industrial scale for real influents.
- New integrations offer greater treatment capabilities and resource efficiency.
- The design of sequential processes is complex and case-specific.
- Sequential processes are highly sensitive to uncertainty and variability.

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ABSTRACT

When direct wastewater biological treatment is unfeasible, a cost- and resource-efficient alternative to direct chemical treatment consists of combining biological treatment with a chemical pre-treatment aiming to convert the hazardous pollutants into more biodegradable compounds. Whereas the principles and advantages of sequential treatment have been demonstrated for a broad range of pollutants and process configurations, recent progresses (2011–present) in the field provide the basis for refining assessment of feasibility, costs, and environmental impacts. This paper thus reviews recent real wastewater demonstrations at pilot and full scale as well as new process configurations. It also discusses new insights on the potential impacts of microbial community dynamics on process feasibility, design and operation. Finally, it sheds light on a critical issue that has not yet been properly addressed in the field: integration requires complex and tailored optimization and, of paramount importance to full-scale application, is sensitive to uncertainty and variability in the inputs used for process design and operation. Future research is therefore critically needed to improve process control and better assess the real potential of sequential chemical–biological processes for industrial wastewater treatment.

Contents

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AOP	advanced oxidation process
MBR	membrane bioreactor
SBR	sequencing batch reactor
AS	activated sludge
SRT	sludge retention time
HRT	hydraulic retention time
COD	chemical oxygen demand
BOD_i	biological oxygen demand after *i* days of incubation
TOC	total organic carbon
DOC	dissolved organic carbon
MLSS	mixed liquor suspended solids
μ	volumetric specific growth rate
μ_m	maximum volumetric specific growth rate
S	substrate concentration
K_s	saturation constant
Y	true yield
k_d	decay coefficient
f_d	cell debris coefficient
IBR	aerobic immobilized biomass reactor
BANF/BAF	sequential biological anaerobic filter and biological aerated filter
CWHPO	catalytic wet hydrogen peroxide oxidation

1. Introduction

The discharge of many of the organic pollutants commonly found in industrial wastewaters (Table 1) is regulated by stringent and specific guidelines [1]. For example, phenolics can be found at concentrations up to 24,000 g m^{-3} in olive-mill wastewater [2], a level 1,600,000-fold higher than the USA monthly average discharge limit for these contaminants [9]. The treatment of such industrial influent is especially challenging due to the inhibitory properties of phenolics, the very high removal performance needed to meet compliance, and the typical high variability of industrial wastewaters [10]. In addition to these challenges, industries face increasing pressures to simultaneously reduce pollutant discharge, water use, and energy consumption. Considerable research efforts are therefore being directed to develop effective, resource-efficient and affordable treatment technologies that specifically target the detoxification of hazardous pollutants. Promising options include variations of 'advanced oxidation processes' (AOPs) via the generation of radicals capable of oxidizing most organic compounds, and targeted biotechnologies relying on specific microorganisms and/or bioprocesses such as membrane bioreactors (MBRs), two-phase partitioning bioreactors (TPPBs), sequencing batch reactors (SBRs), or biofilm reactors. Unfortunately, and in spite of significant progresses in these fields, the literature suggests AOPs are effective but economically prohibitive (Table 2) whereas bioprocesses are comparatively more affordable but often incomplete or difficult to implement (Tables 1 and 2). Hence, when direct biological treatment is not feasible, a cost-efficient alternative consists in using a chemical pre-treatment to convert the hazardous pollutants into more biodegradable compounds [21–24]. This integrated approach, which is *de facto* needed when chemical treatment is incomplete [25], also serves to reduce the consumption of energy and reactants and the indirect environmental impacts associated with chemical treatment [26,27]. Since the principle of sequential chemical–biological treatment was first established by Ollis and co-authors [21–24] in the mid-90s, a large number of studies have demonstrated its potential for a broad range of pollutants and process options [28–31]. The state of the art in this field was reviewed by Oller et al. [30] in 2011, who concluded that further research was critically needed for assessing real wastewater treatment feasibility and costs. Significant progresses have been made since and the technology has now been demonstrated at industrial scale for various real wastewater influents (Table 3). Its costs and environmental impacts have also been preliminarily assessed (Table 2 and Section 4). Sequential chemical–biological treatment processes are therefore 'ripe' for a more in-depth assessment of full-scale potential in consideration of engineering and economic limitations that are not necessarily linked to the presence of the target contaminants (e.g. variability and uncertainty in process inputs and parameters, monitoring and control, etc.) but have not yet been extensively discussed.

With this perspective, this review critically assesses the specific challenges faced during the design and operation of sequential chemical–biological processes treating industrial wastewater laden with recalcitrant and/or inhibitory organic pollutants. Emphasis was given to sequential chemical–biological treatment because this integration is still 'emerging' and unique in that it requires true co-optimization, as explained in Section 3. Sequential biochemical-chemical treatment will not be discussed in this review because this configuration is already implemented at full scale [29,30] and does not, *a priori*, require true co-optimization (i.e. the biological stage is first optimized for cost-efficiency and the chemical stage is added for compliance). For similar reasons, integrated processes where the purpose of the chemical step is to recover/remove pollutants prior/simultaneously to biological treatment (e.g. bioreactors laden with sorbents such as granulated activated carbon) or improve their delivery during biological treatment (e.g. TPBBs) were also excluded from this review (see [31] for more information on these technologies). The exclusions herein listed do not infer any preference in regards to a particular treatment configuration and sequential chemical–biological treatment should generally be selected only after other options have been deemed infeasible (Section 3). Finally, given early research in the field has extensively focused on laboratory-scale demonstration with artificial wastewater, emphasis was given to real wastewater treatment at pilot (semi-industrial) and full (industrial) scales, with the exception of recent laboratories studies with significant findings (e.g. sequential reductive-biological treatment, Section 4). Within this scope, the specific objectives of this review are (i) establish when and why a sequential chemical–biological process should be implemented for industrial wastewater management (Section 2); (ii) summarize the state of the art on the development and applications of sequential chemical–biological treatment processes with focus on recent progresses (Sections 3 and 4); (iii) critically assess the feasibility of sequential treatment processes with regard to variability and uncertainty in input parameters (Section 5); and (iv) identify the most strategic research needs in this field (summarized in Section 6).

Because this review aims to provide information to both experts and non-experts in the field, it was necessary to explain general concepts (Sections 2 and 3, Supplementary information). While this introduces some redundancy with past literature, expert readers can still rapidly access novel findings and discussion because a large amount of background information was disclosed in Boxes 1 and 2 and Supplementary information. The 'core' discussion of this paper thus provides the first direct comparison of the costs of various direct and sequential treatment processes based on recent assessments of real wastewater treatment at pilot- to full-scale (Table 2 in Section 2); a review of recent pilot and full scale demonstrations with real wastewater (Table 3, Section 4) and new process configurations (Section 4); new insights on the mechanisms and potential impacts of microbial community dynamics during sequential process development and operation (Sections 3 and 5,